



MITSURU KUHARA'S **ON THE BECKMANN REARRANGEMENT**

EDITED

BY

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KYOTO

1926

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PREFACE.

It is the editor's privilege, he believes, to lay a short biographical sketch, his own view, of the author of this booklet, before our readers.

Mitsuru Kuhara (久原綱彦) was born in Tsuyama, Mimasaka, November 28, 1855 as the first son of Shūho, the Kuharas have been for generations clan physicians. Upon completion of his studies of science in the College of Science, Tokyo Imperial University, in 1877, he became an assistant in the college. The autumn of 1879 found him a government research fellow at Baltimore, Md. U. S. There he began his experiments in organic chemistry in the laboratory of Professor Ira Remsen who had then just begun his research on an entirely new system, into aromatic compounds at the Johns Hopkins University. During his stay in the laboratory, he derived much inspiration from Professor Remsen's zeal and erudition for the work of his later years. After receiving his doctorate in 1881, returned to Japan, and became assistant-professor of the Tokyo Imperial University, here he continued his investigations relating to the constitution of phthalyl chloride.

In 1886 he became first, professor of chemistry, and in 1894 director, of the First National College (Daiichi Kôtô Gakkô), and thus he contributed largely for twelve years to the education of youth, and the systematizing of the methods of teaching chemistry. Even during such strenuous times he never gave up chemical research, and "A condensation product of acetone and aldehyde ammonia" was one of the fruitful results of his labours in the field of chemistry, by which one can begin to realize his painstaking accuracy and thoroughness.

In 1898 he was appointed, on the founding Kyoto Imperial University, professor of chemistry of the College of Science and Engineering.

The remaining years of his life were spent at the university. Here he was able to carry on his research work more extensively than in the past, as he had a much larger number of co-workers, and the laboratory, putting emphasis on research, was particularly well equipped for advanced study.

Among the noteworthy pieces of work of the earlier years of this period was the one which was reported in the journals of 1900,

"On the synthesis of indigo and its derivatives." Close upon the heels of this investigation, the study of Beckmann's rearrangement, the most prominent endeavor of his life, was undertaken, and in 1907, the first article of the subject was published in the memoirs of the university. The theoretical conviction of Professor Kuhara, strengthened by his experiences with oximes of various types.

In 1903 he became Dean of the Department of Science and Engineering, while since 1901 he was frequently taking general charge of university affairs as Acting-President of the university, becoming President in 1912. Finding that the responsibilities and labours of the presidency of the university, thrust upon him to the detriment of the pursuit of chemistry and to the violation of his own desires and tastes, he resigned, being released from his position in 1913, but retained at the research laboratory as a professor of the Institute of Chemistry.

However, at an age when most men in Japan, are content to rest, retirement from research proved impossible for Professor Kuhara. At sixty he made a fresh start for the investigation of synthetic drugs, and also made further contributions to the Beckmann rearrangement, labours which were being carried on right up to the very day of his death. During the war Professor Kuhara developed an industrial process for the manufacture of salvarsan, which was employed by the newly established Institute for Scientific Research in the university.

He was one of the founders of the Chemical Society of Japan (1878), and was elected first president of the society. In 1891 he received the degree of Rigakuhakushi and was appointed a member of the Imperial Academy in 1906.

He was an excellent teacher and on easy terms with his students, and they worked with him in hearty co-operation, and always engaged in his researches with enthusiasm; and many of the present generation of organic chemists in Japan, being inspired by his noble attitude as a seeker of truth, took up the torch of knowledge to carry it as far as possible, each in his own life, before their own time came to lay it down. Many works on stereochemistry, the mechanism of chemical reactions, colouring matters, and on synthetic drugs have been published in the name of his pupils, and some of these investigations are still being continued and developed further by them.

Those who know the importance of Professor Kuhara's contributions to the science of chemistry, which are shown in the form of a bibliography at the end of the monograph, realise how great a

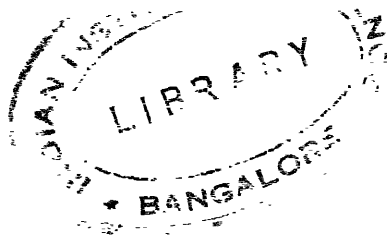
loss the world of science has sustained. We feel that we have already deferred too long the duty of paying some tribute to his memory.

Seven years have elapsed since our great master was stricken down in his home on 21st. of November 1919, and we feel that it is more becoming to bring without further delay an offering, though intrinsically of little value, than to leave his tomb longer without some token of our reverence and love.

In publishing a complete list of his contributions to the molecular rearrangement, collected in this monograph, contributions which have appeared in his laboratory from time to time in the course of many years, the editor is greatly indebted to Professors Riko Majima and M. Kobayashi of the Tohoku Imperial University, who offered advice and suggestions for the publication, and to the editor's colleagues, Drs. B. Masumoto, R. Nakai and C. Tanaka, for their kind help in reading the proofs. The editor wishes also to acknowledge his warm appreciation to the Kyoto Kwagaku Gakushikai for the publication grant.

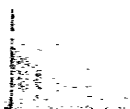
SHIGERU KOMATSU,

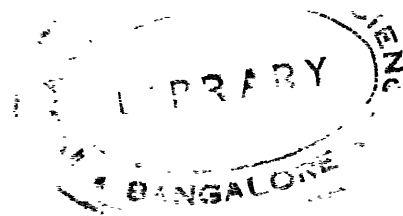
Laboratory of Organic-and Bio-chemistry,
Kyoto Imperial University. June, 1926.



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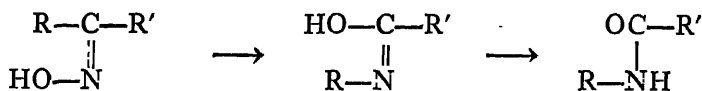


On Beckmann's Rearrangement. I.

By

Mitsuru Kuhara and Tadaka Kainosho.

A well-known intermolecular reaction, so-called Beckmann's rearrangement which especially occurs in the molecules of oximido compounds, is due to the apparent interchange of position between one of two radicals, linked to carbon, and a hydroxyl group united to nitrogen, under the action of acetic acid, its anhydride or chloride, as well as through the action of phosphorus pentachloride and water, etc.; resulting in the formation of the substituted acid amides as final products, as is seen in the following scheme :



The investigation of the cause and mechanism of such rearrangement, has always been one of the problems for chemists ; but it has not yet been satisfactorily solved.

As a matter of fact ; it has already been shown by Beckmann himself and other chemists¹ that the presence of hydrochloric acid greatly facilitates the rearrangement. It may probably act partly as a catalytic agent. For instance : in the case where acetyl chloride is used as a rearranging agent, a small quantity of it is sufficient to convert a large quantity of an oxime into a substituted acid amide ; such rearrangement, as the authors assume, may be due in part to the catalytic action of hydrochloric acid, actually generated from acetyl chloride by reacting with the oxime.²

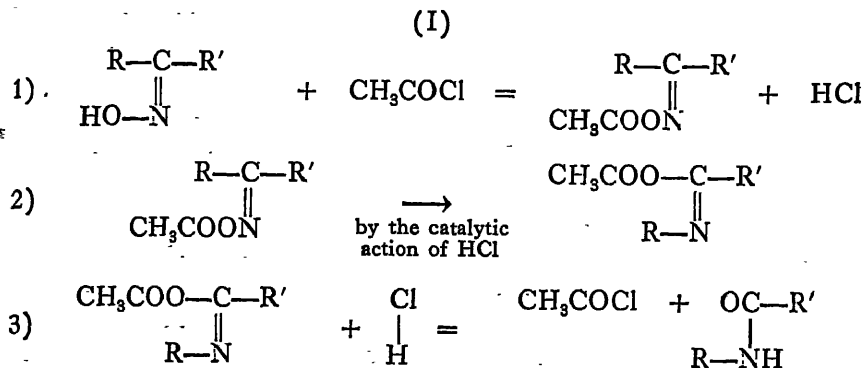
In order to see if there may exist some relation between the amount of an oxime and that of acetyl chloride for the inter-

1 Ber. D. Chem. Gesell., 20, 2581 ; 22, 433 ; 27, 300 ; Amer. Chem. Journ., 18, 754.

2 Compare with Ber. D. Chem. Gesell., 26, 2272 ; 27, 300.

molecular rearrangement of the former, the authors conducted certain experiments by working with a constant quantity of acetyl chloride upon various quantities of diphenyl ketoxime. Thus, 2, 4, and 8 equivalents of diphenyl ketoxime in chloroform solutions were heated with 1 equivalent of acetyl chloride respectively, for ten hours at a temperature of 100° – 110° and it was found in each experiment that the most part of the oxime actually taken, had been transformed into benzanilide. Hence, we have to confess that the amount of the oxime to be rearranged is not dependent upon the amount of acetyl chloride, or it is better to say, that of hydrochloric acid formed in the reaction since it acts as a catalytic agent.

The authors have, now, to put forward an explanation based upon the assumption that the rearrangement of an oxime by acetyl chloride is due to the mutual exchange of the positions between a positive hydrocarbon radical linked to carbon and a negative radical united to nitrogen, in the acetyl oxime produced, arising from the change of the relative affinities analogous to diphenyl ketoximido chloride,¹ facilitated by the catalytic action of hydrochloric acid generated in the reaction, immediately followed by the formation of a substituted acid amide by the further action of hydrochloric acid which may actually take a part of the reaction, as is seen in the following representations :



The acetyl chloride thus formed in the last stage of the reaction may act upon the fresh part of the oxime forming its ester, as before, with the liberation of hydrochloric acid which again may cause the interchange of the positions of two radicals and in turn

¹ Ber. D. Chem. Gesell., 19, 988; 27, 301.

bring about the decomposition of an intermediate product to a substituted acid amide, so the same process progressing further until the oxime is exhausted. A trifling amount of acetyl chloride, therefore, must be theoretically possible to convert an infinite quantity of the oxime into a substituted acid amide, apparently acetyl chloride remaining unchanged.

Admitting that hydrochloric acid may actually take a part of the reaction in such a way as already stated, it is to be presumed that when various quantities of hydrochloric acid is allowed to act upon the same definite quantity of a pure oxime ester, the quantities of a rearrangement product or substituted acid amide produced, should be proportional to those of the hydrochloric acid taken, if its quantities be smaller than enough to be equivalent to those of the oxime ester used, as the formation of new hydrochloric acid will not be effected in the case of the ester, the acetyl chloride formed remaining by itself unchanged, but to the quantities of oxime ester, if hydrochloric acid be present more than enough to be equivalent to those of the oxime ester. For the experiments, the authors studied the action of various molecular proportions of hydrochloric acid in its saturated chloroform solution upon a constant molecular quantity of acetyl diphenyl ketoxime, $(C_6H_5)_2C:NO \cdot COCH_3$, by heating each mixture in a sealed tube at a definite temperature for the same period of time, and found in fact the production of benzanilide to be approximately proportional to the actually reacting quantities of hydrochloric acid used, as is seen in the following table:

$(C_6H_5)_2C:NO \cdot COCH_3$ (used).	HCl (used).	$C_6H_5 \cdot CONH \cdot C_6H_5$ (produced).	$C_6H_5 \cdot CONH \cdot C_6H_5$ (to be produced theoretically).
1 mol.	2 mols.	1 mol. approximately.	1 mol.
1 „	1 mol.	1 „ „	1 „
1 „	0.5 „	0.5 „ „	0.5 „
1 „	0.25 „	0.25 „ „	0.25 „
1 „	0.20 „	0.20 „ „	0.20 „

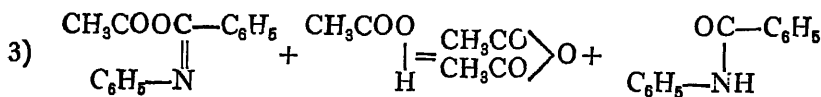
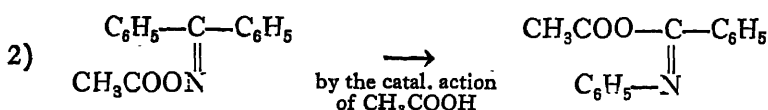
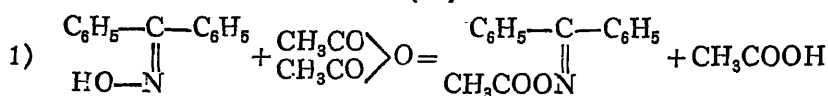
Details will be referred to in the Experimental Part.

With regard to the rearrangement of the oxime by acetic anhydride and by glacial acetic acid, we find in Beckmann's experiments¹ that diphenyl ketoxime undergoes the rearrangement by the large excess of either of those two agents at 180° with the production of

¹ Ber. D. Chem. Gesell., 20, 2580.

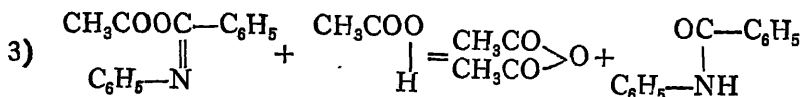
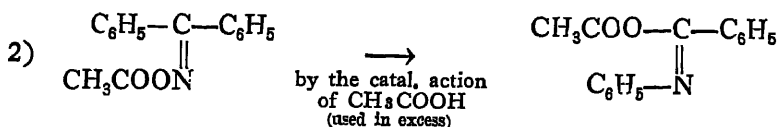
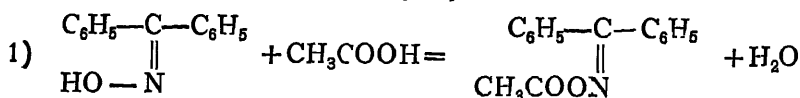
a small quantity of benzanilide, the decomposition of a greater part of the oxime taking place. In this case, acetyl diphenyl ketoxime, which ought to be formed from diphenyl ketoxime by interacting with either of these two agents, may actually undergo the rearrangement either by the catalytic action of acetic acid produced in the reaction or by one being used in excess, but slowness of the rearrangement may be attributed to the feeble catalytic action of acetic acid, due to the weakness of its acidity; nevertheless the mechanism may be analogous to that with acetyl chloride, thus:

(II)



Acetic anhydride formed in the last stage may successively act upon a fresh part of the oxime, it being possible for the reaction to progress further.

(III)

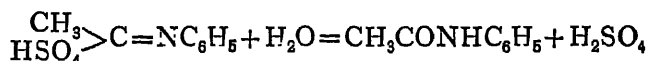


According to Beckmann's experiments,¹ a mixture of glacial acetic acid and acetic anhydride saturated with hydrochloric acid, was

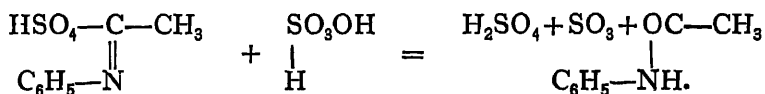
¹ Loc. cit.

found to cause the molecular rearrangement of diphenyl ketoxime and of methyl phenyl ketoxime more readily at much lower temperature, say 100° , than that at which acetic acid or acetic anhydride alone exerts its respective action as stated just above. Now, the authors maintain that hydrochloric acid, which is much stronger in its acidity than acetic acid, will act as a catalytic agent upon the acetyl esters of the oximes, so that the interchange of the positions of the phenyl and the acetic acid radicals may take place readily, and, therefore, the reaction is very likely to follow the mechanism I. already given.

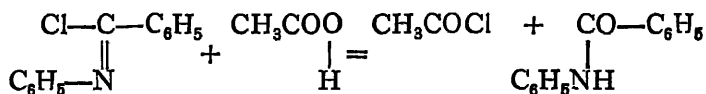
The rearrangement of the oxime by sulphuric acid seems to take place more readily than by acetic acid itself. According to Beckmann¹ methyl phenyl ketoxime (also diphenyl ketoxime) undergoes the rearrangement, at 100° , with five times its weight of conc. sulphuric acid, the final stage of which is stated to be dependent upon the decomposition of an intermediate product by water used, as is seen :



It is, however, very probable that, by applying the analogy to this case, the decomposition of an intermediate product may be caused by sulphuric acid itself, just as in the case of other acids previously described, already resulting in the formation of benzanilide before the use of water, as is seen :



With regard to the decomposition of an intermediate product by acid, the authors carried out an experiment with benzanilimido chloride, formed from diphenyl ketoxime by phosphorus pentachloride. When the chloride, prepared by the method stated by Beckmann,² was allowed to interact with glacial acetic acid mixed with some acetic anhydride, the formation of acetyl chloride and benzanilide immediately took place ; hence the reaction may be :



Now, the authors, in conclusion, venture to express the opinion that, after all, it is possible the rearrangement of the oxime by acetyl

¹ Ber. D. Chem. Gesell., 20, 1507.

² Ibid., 19., 988.

chloride, acetic acid, acetic anhydride, and sulphuric acid, may all be founded upon analogous mechanism, (though Beckmann doubts the formation of analogous intermediate products in all cases),¹ but its rate may depend upon the degree of acidity of the hydrochloric, sulphuric, or acetic acid, which plays a part in the rearrangement process, just as the commonly accepted view of the catalytic action of acids shows. The relative strength² of these acids as is shown in the following table, by arranging them in the order of their electric conductivity in their equivalent solutions, and of the mean value of the velocity constant of sugar inversion and catalysis of methyl acetate :

	Velocity constant,	Electric conductivity.
Hydrochloric acid	100	100
Sulphuric acid	54	65.1
Acetic acid	0.4	0.4

seems to be concordant with the relative readiness of the rearrangement of the oximes by those acids.

EXPERIMENTAL PART.

I. *Action of Acetyl Chloride upon Diphenyl Ketoxime.*

Different quantities of diphenyl ketoxime were allowed to interact with a smaller, definite quantity of acetyl chloride, and it was observed as a fact that the action of acetyl chloride, so as to cause the rearrangement of the oxime, is independent of the amount of the latter present. In the experiments, 1.39, 2.78, and 5.55 grams of diphenyl ketoxime, or its 2, 4, and 8 equivalents respectively, were mixed with 0.276 gram of acetyl chloride, or its 1 equivalent, dissolved in 5 c. c. of anhydrous chloroform, and heated in a sealed tube at 100°-110° for ten hours. The content of the tube was evaporated to dryness, when acetyl chloride was noticed by its characteristic odor as being all present; and the residue was treated with hot alcohol. On evaporating the alcoholic solution, the impure benzanilide was left as a residue, which was crystallized from hot benzene and then washed twice with petroleum ether. The benzanilide so obtained was dried and weighed; it may show approximately the whole amount of the

1 Ber. D. Chem. Gesell., 27, 301.

2 Walker's Phys. Chem., (ed. 1901), P. 279.

rearrangement product, the results being represented in the following table :

Number of experiment.	Diphenyl ketoxime		Acetyl chloride		Benzanilide formed	
	taken in gram.	in terms of equivalent.	taken in gram	in terms of equivalent.	in gram.	per cent.
I.	1.39	2.	0.276	1.	1.09	78.4
II.	2.78	4.	0.276	1.	2.19	78.8
III.	5.55	8.	0.276	1.	4.13	74.4

By inference from the above data, the action of acetyl chloride, or possible of hydrochloric acid generated, should be merely catalytic, as comparatively a small quantity of acetyl chloride is able to effect the rearrangement of the most part of the oxime present, no matter how large the quantity of the latter may be.

2. *Action of Hydrochloric Acid upon Acetyl Diphenyl Ketoxime.*

2.5 grams of acetyl diphenyl ketoxime¹ dissolved in some chloroform saturated with dry hydrochloric acid, was heated in a sealed tube at 130° for fifteen hours. The content of the tube, when cooled, was found to assume a slightly brown colour, with some white, scaly crystals suspended on the surface of the liquid. The whole content was subjected to distillation over a water bath, and in the distillate was observed the presence of acetyl chloride, confirmed by its odor as well as by converting it into acetyl-o-toluide. The residue was treated with alcohol, in which it dissolved almost completely, and the solid left behind on evaporating the alcoholic solution (during which process the characteristic odor of acetic and benzoic esters was noticed) was washed with water and then boiled with a 20% solution of caustic potash to remove the oxime and benzoic acid present, and finally dissolved in chloroform, from which solution the white, scaly crystals separated out. The crystals melted at 159° and had all the

1 The authors found it more advantageous to use acetic anhydride for the acetylation of diphenyl ketoxime, while Spiegler recommends the use of acetyl chloride (Monatsh. f. Chem., 5, 205) by which process a greater part of the oxime undergoes rearrangement, as the authors observed. The acetyl diphenyl ketoxime prepared by this method was analysed and its melting point found to be 71°, while Spiegler states it to be 55°.

properties of benzanilide. The aqueous washing, acidified with hydrochloric acid, was found to contain a minute quantity of ammonium chloride and hydroxylamine hydrochloride, and a trace of aniline hydrochloride recognizable by Runge's reaction. From this experiment, it is obvious that, in the rearrangement of the oxime, the formation of its ester and the action of hydrochloric acid are the most necessary conditions.

Next, in order to confirm the opinion that hydrochloric acid must actually take part in the reaction for the decomposition of an intermediate product, the authors conducted experiments in the way described below: Different molecular quantities of hydrochloric acid in chloroform solution were allowed to act upon a certain definite molecular quantity of acetyl diphenyl ketoxime, that is 2, 1, $\frac{1}{2}$, $\frac{1}{4}$, etc., of the former in terms of mol. to 1 of the latter, in sealed tubes at 120°–150° for fifteen hours. The content of each tube was subjected to distillation, and the distillate was found to contain some acetyl and benzoyl chlorides as in the previous experiment, the presence of the latter being due, perhaps, to the secondary reaction. The residue was treated with hot alcohol, and, on distilling the alcoholic solution so obtained over a water bath, some acetic and benzoic esters were observed to pass over. The residual substance was washed with hot water three times, and the washing, which had been acidified with hydrochloric acid, contained a minute quantity of ammonium chloride, hydroxylamine hydrochloride, and a trace of aniline hydrochloride, as in the above experiments. The solid left after washing with hot water, consisting of benzanilide and some diphenyl ketoxime, was washed several times with a hot 20% solution of caustic potash, and then repeatedly with water until the alkaline reaction disappeared in the washing. It was, now, perfectly dried and again washed with petroleum ether, and then weighed as the approximate amount of the rearrangement product or benzanilide after drying, as it is difficult to effect the rearrangement of the whole oxime ester and to get the product in pure state. The results of the experiments are given below:

On Beckmann's Rearrangement. I.

The first series of experiments : heated for 15 hours at 150°.

Number of experiment	Acetyl diphenyl ketoxime	Hydrochloric acid	Acetyl diphenyl ketoxime	Hydrochloric acid	Benzanilide found	
	taken in gram.	taken in gram.	in terms of mol.	in terms of mol.	in gram.	in terms of mol.
I.	0.720	0.210	1.	2.	0.407	0.716
II.	1.440	0.210	1.	1.	1.034	0.935
III.	1.440	0.105	1.	0.5	0.605	0.533
IV.	2.880	0.105	1.	0.25	0.733	0.323

The second series of experiments : heated for 15 hours at 130°.

V.	0.864	0.063	1.	0.5	0.371	0.544
VI.	1.728	0.063	1.	0.25	0.359	0.263
VII.	1.440	0.042	1.	0.20	0.249	0.219

The third series of experiments : heated for 15 hours at 120°.

VIII.	1.445	0.320	1.	1.518	0.930	0.816
IX.	2.890	0.320	1.	0.759	1.703	0.747
X.	1.445	0.080	1.	0.380	0.475	0.418
XI.	2.320	0.128	1.	0.367	0.690	0.379

As is seen in the tables, in each experiment, except I and VIII, approximately as many mol, of benzanilide as of hydrochloric acid used, has been produced as the rearrangement product; but in experiments I and VIII the quantity of hydrochloric acid having been present in excess, that is more mol. than correspond to that of acetyl diphenyl ketoxime, the yield of benzanilide in each exhibits the approximation toward the mol. of acetyl diphenyl ketoxime taken. In the latter case, however, the yield of benzanilide, which ought to be 1 mol. theoretically in each experiment, corresponding to 1 mol. of acetyl diphenyl ketoxime, is little too low; such deviation, the authors think, may be attributed to the secondary decomposition of the oxime ester owing to the presence of hydrochloric acid in excess.

3. Action of Acetic Acid upon Benzanilidimido Chloride.

To a petroleum ether solution of benzanilidimido chloride, pre-

pared according to Beckmann's statement,¹ some glacial acetic acid mixed with $\frac{1}{3}$ its volume of acetic anhydride was added and the mixture vigorously shaken. Petroleum ether was then quickly expelled by warming with hot water, leaving behind the hot acetic acid solution which, on cooling, separated scaly crystals. The crystals melted at 160° and had all the properties of benzanilide. Hence it is evident that an intermediate product in the rearrangement of the oxime ester is decomposed by acetic acid and, perhaps, by other acids into substituted acid amide, but not by hydrochloric acid in this case because the intermediate product contains no oxygynated negative radical.

Further experiments are being carried on with some other oximes; and the authors expect to communicate the results before long.

March, 1907.

1 Ber. D. Chem. Gesell., 19, 988.

On the Beckmann Rearrangement. II.

BY

Mitsuru Kuhara and Yoshinori Todo.

For the explanation of the Beckmann rearrangement, several theories have been proposed up to this time by different chemists, but none of them is likely to lead to a satisfactory generalization owing to the present incomplete state of investigation.¹

By the measurement of the velocity in the rearrangement of methylphenylketoxime through the action of sulphuric acid, which was performed by Sluiter² by determining the amount of acetic acid, liberated from acetanilide formed in the reaction, by its saponification, there was obtained a constant which shows the reaction to be monomolecular. The author's attention was directed to the same line of investigation in a somewhat different way, by ascertaining the influence of different acid chlorides upon the rate of rearrangement of diphenylketoxime, and the velocity of its rearrangement by acetyl chloride as well as that of acetyldiphenylketoxime by hydrochloric acid.

For the study of the influence of different acid chlorides, acetyl, monochloroacetyl and benzenesulphonyl chlorides were taken. In each experiment, acid chloride and diphenylketoxime were allowed to react on each other in molecular proportions at 60°, each substance having been dissolved in chloroform so as to make $\frac{1}{2}$ molar solution. After a definite interval of time, the benzanilide produced was carefully isolated and its quantity determined. The following table shows

1 Beckmann, Ber. D. Chem. Gesell., 27, 300. Stieglitz, Amer. Chem. Jour., 18, 751; 29, 49. Nef, Ann. d. Chem., 318, 227. Slosson, Amer. Chem. Jour., 29, 239. Werner and Piquet, Ber. D. Chem. Gesell., 37, 4295. Sluiter, Rec. trav. chim., 24, 372. Wallach, Ann. d. Chem., 346, 272. Diels and Stern, Ber. D. Chem. Gesell., 40, 1631. Schröter, *ibid.*, 42, 2336. Stieglitz and Peterson, *ibid.*, 43, 782. Montagne, Rec. trav. chim., 25, 376; Ber. D. Chem. Gesell., 43, 204.

2 Rec. trav. chim., 24, 372.

the comparative amounts of benzanilide formed from diphenylketoxime by different acid chlorides :

Time (min.).	% Benzanilide formed		
	by acetyl chloride.	by monochlor- acetyl chloride.	by benzene- sulphonyl chloride.
10	0	61.0	93.2
15	2.4	—	—
30	9.4	66.1	—
60	26.9	70.7	—
90	37.2	74.9	—
120	43.9	76.9	—

As seen from the table, diphenylketoxime did not change at all into benzanilide by acetyl chloride in 10 min., but in 15 min. only 2.4%, while by monochloracetyl chloride more than $\frac{1}{2}$, and by benzenesulphonyl chloride nearly all of its quantity suffered rearrangement in 10 min. Hence, the rate of rearrangement must be dependent upon the degree of acidity of the acid from which a chloride is derived, in other words, upon the nature of the negative character of the acid residue, $R'COO-$, coupled in oxime ester that may be formed by acid chloride. Thus, the relative strengths of acetic, monochloracetic and benzenesulphonic acids from which 3 respective chlorides are derived, as arranged in the order of their dissociation constants, are found to be concordant with the rate of rearrangement :

Acids.	K.
Acetic acid	0.000018
Monochloracetic acid	0.001550
Benzenesulphonic acid	Immeasurably great.

For the measurement of the velocity of rearrangement of diphenylketoxime which would be effected by acid chloride, the authors took acetyl chloride and diphenylketoxime in molecular proportions and dissolved each in dry chloroform so as to make $\frac{1}{2}$ molar solution at 60°. Both solutions, taken in 5 c.c. each and mixed in a sealed tube at 0°, were allowed to remain in a thermostat at the temperature of 60°. After a certain interval of time, the sealed tube was taken out from the thermostat, and its contents transferred into

a beaker, and the chloroform removed by blowing dry air through the solution. Before setting the sealed tube in a thermostat, and after removing it from the same, it was kept in ice cold water in order to arrest the progress of reaction. The residue obtained by the evaporation of chloroform was treated with 20% solution of sodium hydroxide, filtered and washed well with water. The benzanilide left a residue by such a treatment was dissolved in alcohol, and the solution then filtered was allowed to evaporate. The residue consisting of benzanilide was dried at 110° and its weight ascertained. By such a process of treatment, we were able to isolate from the products all of benzanilide in a pure state, which was judged from its right melting point of $158-159^{\circ}$.

Inferring the nature of reaction from the results of experiment, the change would actually belong to the type of monomolecular reaction, as a velocity constant has been obtained by the calculation with the well-known equation for that of the first order,

$$0.4343 k = \frac{1}{t} \log \frac{a}{a-x}$$

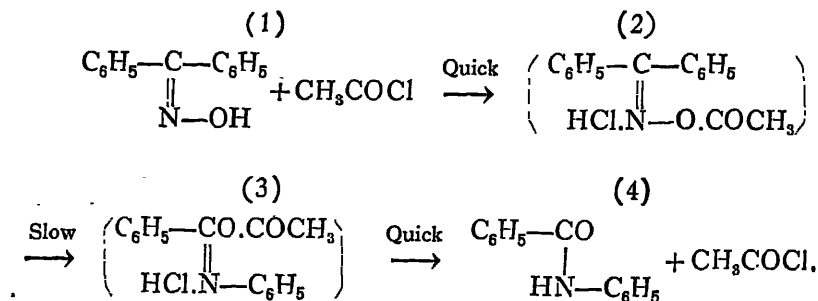
as will be shown in the following table, the initial disturbance being possibly due chiefly to the influence of the temperature of the contents in the sealed tube which must take a certain interval of time to be equalized with that of the thermostat.

t (min).	x .	$\frac{1}{t} \log \frac{a}{a-x}$.	$\frac{1}{t-15} \log \frac{a-x_{15}}{a-x}$.
15	2.4	0.00070	
30	9.4	0.00143	0.00215
40	14.9	0.00175	0.00238
50	20.6	0.00200	0.00256
60	26.9	0.00227	0.00228
90	37.2	0.00224	0.00229
120	43.9	0.00209	0.00213
180	61.0	0.00227	0.00241
240	69.0	0.00212	0.00221
360	78.2	0.00184	0.00188
480	88.9	0.00198	0.00203
		0.00210	0.00223

Moreover, the rearrangement of acetyldiphenylketoxime by hydrochloric acid has been studied. For this purpose, acetyldiphenylketoxime was dissolved in a saturated solution of hydrochloric acid in chloroform at 0°, whose strength had previously been ascertained by titration, in such a way as to correspond to each other in molecular proportions. 10 c.c. of the solution were taken, and heated in a sealed tube by immersing into a bath of boiling water. After a certain interval of time, the content of the tube was treated in the same way as in the previous experiments, and the quantity of benzanilide produced was determined. As will be seen in the results here stated in the following table, the reaction is also of monomolecular type.

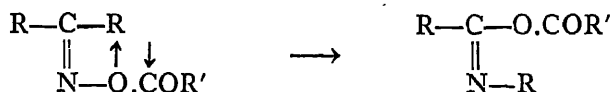
t (min.).	x .	$\frac{1}{t} \log \frac{a}{a-x}$.
20	27.4	0.00695
30	37.5	0.00680
40	44.3	0.00635
60	56.1	0.00596
90	76.4	0.00697
120	80.0	0.00583
		0.00648

Interpreting the mechanism of rearrangement from the statements so far recorded, the authors propose for its explanation to represent the change by the following scheme with modification to the previous one¹:

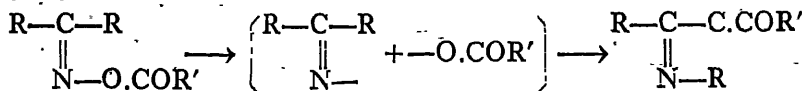


As the authors have to regard the scheme by Sluiter¹ with respect to the progress of rearrangement as correct, in the present case by analogy the change of the system (1) to (2) is regarded as quick, (2) to (3) as slow and (3) to (4) as quick, and as a consequence only the velocity in the second phase of reaction ((2)) to ((3)) should be measurable; therefore, the nature of reaction in the rearrangement must be observed to be monomolecular as a matter of course. The view on the mechanism of rearrangement, proposed as above, may further be explained, based upon the assumptions which will be described hereinafter.

1. Rearrangement of ketoxime may be due to an interchange of positions between a hydrocarbon radical linked to carbon and an acid residue attached to nitrogen in an oxime ester formed in reaction :



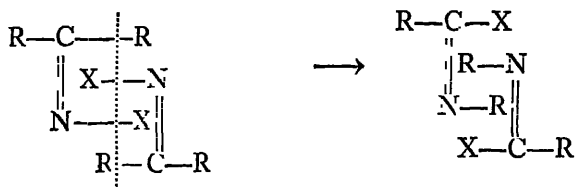
As the primary cause of such an interchange, the authors take account of the tendency of an acid residue to separate from nitrogen which, when has been strengthened under the influence of temperature, but in some cases by a joint action with acid, may cause its dissociation,² by which the shifting of a hydrocarbon radical to nitrogen by its effort to occupy a more favoured position, and as a consequence the transposition of the acid residue to carbon are possible to be brought about; therefore the change may be looked upon as the effect of a process may be looked upon as the effect of a process like double decomposition, which takes place within a molecule or between 2 molecules :



1 Loc. cit.

2 Nef has applied his theory of dissociation to the explanation of the Beckmann rearrangement, but its scheme is different from that proposed by the authors.—*Ann. d. Chem.*, 318, 227. According to Beckmann's view, the process consists in the transposition of electrically charged radicals or ions, but the reagent merely acts as a catalyser by increasing the velocity of interchange.—*Ber. D. Chem. Gesell.*, 27, 300.

or



in which $\text{X}=\text{R}'\text{CO.O.}$ —.

Such a mobility of acid residue is considered to stand in a close connection with the strength of its negative character, that is, the more negative the acid residue the looser may be its linking to nitrogen, rendering the system more liable and more prone to rearrangement; hence it is regarded that in the rearrangement of diphenylketoxime by acetyl, monochloracetyl and benzenesulphonyl chlorides, the acid residues $\text{CH}_3\text{CO.O'}$, $\text{CH}_2\text{ClCO.O'}$, and $\text{C}_6\text{H}_5\text{SO}_2\text{O'}$ in their respective ethers may change their positions more or less readily, in proportion to the strength of their negative character, namely in the order of benzenesulphonyl, monochloracetyl and acetyl oximes, as the experiments on the rate of rearrangement show.

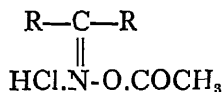
Beckmann¹ states that diphenylketoxime and methylphenylketoxime yield, by the action of acetyl chloride, their acetyl ethers, which at all events undergo rearrangement, when hydrochloric acid, liberated in the reaction, is allowed to come completely to action; and also it has been shown by one of us and Kainosho,² as well as by the authors that pure acetyldiphenylketoxime actually needs the presence of hydrochloric acid for its rearrangement, while several oximes³ such as diphenylketoxime, benzamidoxime, benziloximes, etc. readily undergo rearrangement in presence of alkali or pyridine by the action of benzenesulphonyl chloride, although hydrochloric acid liberated in the reaction is immediately removed by alkali or pyridine. Hence, in the case of acetyl oximes, hydrochloric acid must be a necessary reagent for rearrangement, but in the case of benzenesulphonyl oximes, the transposition of the benzenesulphonic acid residue may simply be effected without the aid of hydrochloric acid. For such a difference of the behaviors of acetyl and benzenesulphonyl oximes, the authors put forward an explanation based upon the assumption that in benzenesulphonyl oxime, the benzenesulphonic acid residue, $\text{C}_6\text{H}_5\text{SO}_2\text{O'}$, may readily separate from nitrogen on account of its strong negative

1 Ber. D. Chem. Gesell., 27, 2583.

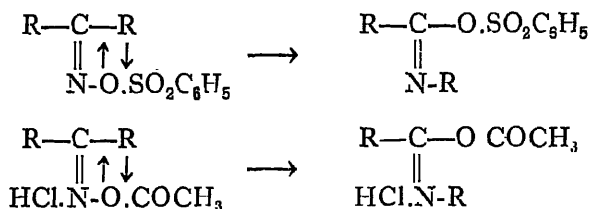
2 The Memoirs, Vol. I, 254 (P. 1).

3 Ber. D. Chem. Gesell., 24, 3539, 4162, 4167; 37, 4295.

character, while in the case of acetyl oximes, their hydrochlorides,



may be formed on account of the relatively weak negative character of the acetic acid residue, $\text{CH}_3\text{CO.O}'$, but the latter group getting more negative under the influence of hydrochloric acid added to nitrogen may increase its tendency to separate from the latter; and eventually its migration may be effected:



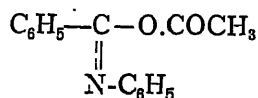
It has been noticed by the authors, as already stated, that at the temperature of 60° , the rearrangement of diphenylketoxime by the action of acetyl chloride progresses moderately, while that of pure acetyldiphenylketoxime by hydrochloric acid is exceedingly slow but very rapid at the temperature of boiling water, although in both cases the hydrochloride of acetyldiphenylketoxime ought to suffer the change equally under the same condition. The authors have now to explain such a phenomena by assuming that in the former case the elements of hydrochloric acid may act in a nascent state upon acetyldiphenylketoxime formed in the reaction, yielding its hydrochloride, but in the latter the hydrochloric acid present in a free state may need high temperature for the formation of the salt.

2. It is evident from the experiments by one of us and Kainoshō¹ that hydrochloric acid may actually take part of reaction in the change of acetyldiphenylketoxime formed as an intermediate product in the rearrangement of diphenylketoxime, because as a matter of fact, hydrochloric acid and acetyldiphenylketoxime have to react on each other always in equivalent proportions. Thus, their experiments show that when the different quantities of hydrochloric acid are allowed to act upon the same definite quantity of pure acetyldiphenylketoxime, the quantity of the resulting benzanilide is equal-

1 The Memoirs, Vol. I, 254 (p. 1).

ent to that of hydrochloric acid taken, if its quantity is smaller than enough to be equivalent to that of the oxime ester used, as the formation of new hydrochloric acid is not effected in the case of the ester, the acetylchloride produced remaining unchanged, but to the quantity of oxime ester if hydrochloric acid is present more than enough to be equivalent to that of the oxime ester. Such a relation of the interacting substances, therefore, stands in harmony with the assumption in respect to the second and third phases of the reaction in rearrangement, as is seen from the scheme of mechanism already represented.

3. In this laboratory, S. Kodama has lately succeeded in isolating a compound which must possess a constitution corresponding to the formula,



by treating benzimidochloride, $\text{C}_6\text{H}_5-\text{CCl}=\text{N}-\text{C}_6\text{H}_5$, with silver acetate. It is a thick yellow oily substance of unstable nature. By passing dry hydrochloric acid through its ethereal solution cooled with a freezing mixture, its hydrochloride separates out as a canary yellow precipitate, but by the excess of the acid changes to acetylbenzanilide¹ and other compounds by molecular rearrangement. The hydrochloride dissolved in chloroform and heated in a sealed tube above 60° , yields benzanilide at once; hence its decomposition is assumed to correspond to the last phase of the process of rearrangement. Matter about that compound has not been published yet, as its investigation is now going on.

September, 1910.

1 O. Mumm states that he has obtained acetylbenzanilide by treating benzimidochloride with sodium acetate, but nothing is said about such a compound as Kodama has prepared.—*Ber. D. Chem. Gesell.*, 43, 886.

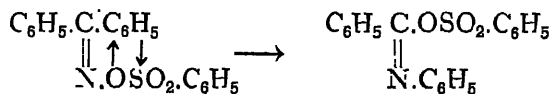
On the Beckmann Rearrangement. III.

By

Mitsuru Kuhara and Teppei Okada.

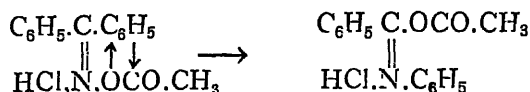
An explanation for the mechanism of the Beckmann rearrangement has been brought forward by one of us and Todo in their recent article¹, based upon the assumptions that the primary cause of rearrangement consists in the dissociation of an acid residue from nitrogen in the oxime ester formed in reaction, and as its consequence an interchange of positions between a hydrocarbon radical linked to carbon and an acid residue attached to nitrogen may be effected, and that such a mobility of the acid residue may stand in a close connection with the strength of its negative character, since in the case of the acetyl oximes rearrangement is hardly brought about by heat alone when an acid such as hydrochloric acid is not present, while in the case of the benzenesulphonyl oximes rearrangement is spontaneously effected.

Now the presence of the acid residue must be a necessary condition of the Beckmann rearrangement; it is then assumed that the oximes would at first yield their esters, say by acid chlorides, and subsequently an acid residue and a hydrocarbon radical may exchange their positions, the dissociation primarily taking place in the case of the oxime esters containing the residue of strong acid without the aid of any reagent, sometimes by mere elevation of temperature, while in the case of the esters containing the residue of weak acid the tendency to dissociate may be accelerated by the aid of hydrochloric acid forming their hydrochlorides, or by its joint action with heat; as has been already pointed out²:



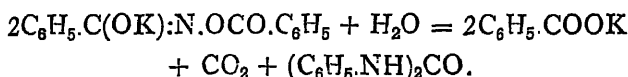
1 Mem. Coll. Sci. Engin., Kyoto, 2, 387 (1909-1910) (p. 11).

2 *Ibid.*, 2, 394 (1909-1910) (p. 17).

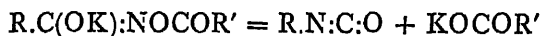


Admitting the presence of the acid residue in the oxime as a necessary condition of rearrangement, the several facts relating to the decomposition of dihydroxamic acids may be regarded as giving a support to the authors' view.

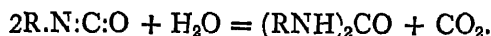
Lossen and Rotermund¹ have shown that the neutral potassium salt of dibenzhydroxamic acid in its aqueous solution gives benzoic acid, carbon dioxide and diphenylurea on standing by itself or by heating:



Thiele and Pickard² have also pointed out that in the rearrangement of potassium salts of dihydroxamic acids the splitting up of a salt into an isocyanate and a potassium salt of the acid related to the acid residue linked to the nitrogen of the oxime group must be brought about at first:



and then the formation of a symmetrical disubstituted urea would take place by the interaction of the isocyanate formed and water:



The free dihydroxamic acids also yield the analogous products of decomposition by heating at high temperature or by dry distillation.³

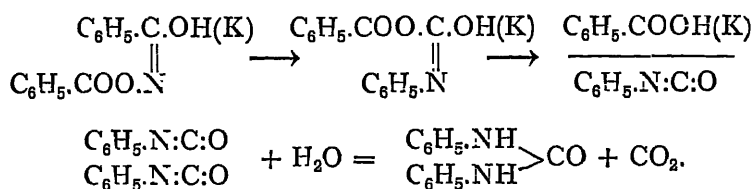
The authors have now to assert that in those cases of decomposition of dihydroxamic acids and their salts through the Beckmann rearrangement which is, we believe, wholly dependent upon the presence of acid residue, the interchange of positions between an acid residue and a hydrocarbon radical must occur, being preceded by the dissociation of the former as the primary cause of rearrangement, and resulting in the formation of an acyl derivative of a substituted im-

1 Lieb. Ann., 161, 359 (1872); 175, 257 (1875).

2 Ibid., 309, 189 (1899).

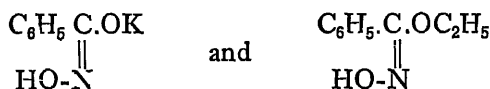
3 Ibid., 175, 311, 312 (1875); 309, 189 (1899); Ber. D. Chem. Ges., 27, 1256 (1894).

inocarbonic acid as an intermediate product which would break up into an isocyanate and an acid or salt, and finally in the production of a disubstituted urea by the action of water upon the isocyanate; then, taking as an example the decomposition of dibenzhydroxamic acid and its potassium salt, the course of reaction should be represented as follows¹:



Thus, in the rearrangement of several other dihydroxamic acids and their potassium salts² which behave similarly as dibenzhydroxamic acid and its potassium salt, giving the analogous decomposition products under an analogous condition, the mechanism of reaction should be analogous.

The authors repeated Lossen and Rotermund's³ experiment, by distilling an aqueous solution of the neutral potassium salt of dibenzhydroxamic acid, and also observed the production of aniline which must be due to the formation of diphenylurea, caused by the Beckmann rearrangement owing to the presence of the benzoic acid residue. We could, however, not find even a trace of aniline from the potassium salt of benzhydroxamic acid and from ethylsynbenzhydroximic acid⁴:



by distilling an aqueous solution of the former, and by heating the latter above its melting point for several hours and then distilling the product with aqueous alkali. This makes it evident that the Beckmann rearrangement would not take place in the salt and ester of benz-

1 Such a scheme of reaction is seen in Meyer and Jacobson's *Lehrbuch d. org. Chemie*, 1st ed., II, 560, but nothing is said about the essence which may lead to rearrangement.

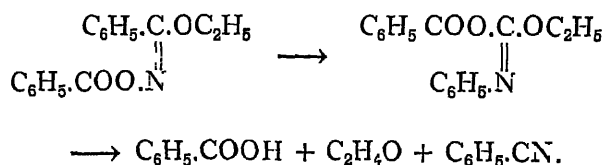
2 *Lieb. Ann.*, **175**, 311, 312 (1875); **309**, 189 (1899); *Amer. Chem. J.*, **48**, 1 (1912).

3 *Ibid.*, **161**, 359 (1872); **175**, 257 (1875).

4 *Ber. D. Chem. Ges.*, **25**, 37 (1892).

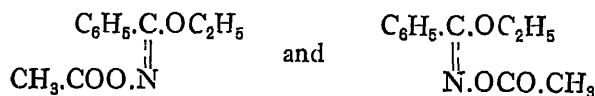
hydroxamic acid, for the necessary acid residue is lacking in each. Also, the facts already observed by Hantzsch¹ appear to give a further support to the authors' view. He has shown that by gently warming the potassium carbonate solution of acetylbenzhydroxamic acid, $C_6H_5.C(OK):N.OCO.CH_3$, diphenylurea abundantly separates out, while with the potassium carbonate solution of free benzhydroxamic acid, $C_6H_5.C(OK):N.OH$, no such a decomposition takes place even by boiling. The authors, now, dare to explain by ascribing such a difference of the behaviours of two compounds to the presence and absence of the acetic acid residue in acetylbenzhydroxamic and benzhydroxamic acids respectively.

It is already known that ethyl dibenzhydroxamate of the syn form (i.e., ethylsynbenzhydroxamic acid benzoyl ester)² is decomposed into benzonitrile, benzoic acid and acetaldehyde by heating above its melting point; and the reaction has been pointed out as follows³:



So, we declare that in the case of ethylsynbenzhydroxamic acid benzoyl ester, the Beckmann rearrangement should take place, for it may be regarded as the ethylbenzhydroxamic acid derivative containing the benzoic acid residue linked to nitrogen in the syn form.

In order to get a further confirmation for the authors' view, two isomeric acetyl esters of ethylbenzhydroxamic acid⁴:



were heated above their melting points for some hours, and the product from each ester was subjected to steam distillation in alkaline solution, as in the experiment of ethylbenzhydroxamic acid. By such

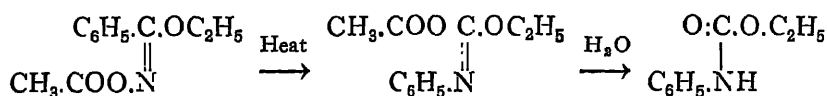
1 Ber. D. Chem. Ges., 27, 1257 (1894).

2 Lieb. Ann., 205, 279 (1880); Ber. D. Chem. Ges., 25, 44 (1892).

3 Meyer and Jacobson's Lehrbuch d. Org. Chemie, 1st ed., II, 561.

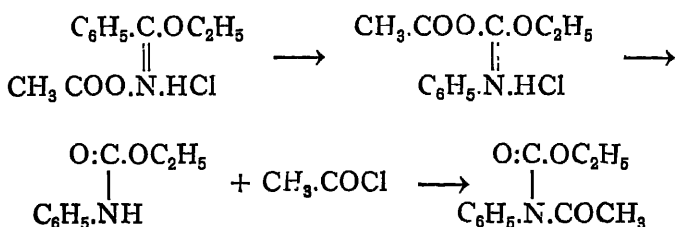
4 Ber. D. Chem. Ges., 25, 40-41 (1892).

a treatment a small quantity of aniline was found to be formed from the syn acetyl ester, but not a trace from the anti ester; so the production of aniline may be due to the decomposition of urethane somewhat formed from the syn ester as the result of the Beckmann rearrangement by heat, the reaction being assumed to be:



Such a course of reaction as we assume, and that for the production of phenylurethane from ethylsynbenzhydroxamic acid by phosphorus pentachloride and water, which has been pointed out by Werner¹, should be no doubt same in essence.

Moreover, each of two isomeric acetyl esters was heated in a sealed tube, dissolved in chloroform saturated with hydrochloric acid, at the temperature of 100–102° for twelve hours. The product from the syn acetyl ester was observed to contain phenylurethane and acetyl phenylurethane, but that from the anti ester not at all. The authors, then, admit it as correct that in the case of the syn acetyl ester the Beckmann rearrangement is accelerated by the aid of hydrochloric acid, just as has been shown in the rearrangement of the acetyl ester of diphenylketoxime², thus being represented as follows:



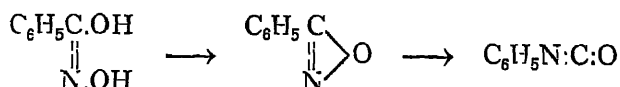
Lossen³ has announced that benzhydroxamic acid and its barium salt decompose into aniline and carbon dioxide by dry distillation. According to his statement, rearrangement actually takes place in

1 Ber. D. Chem. Ges., 25, 39 (1892).

2 Mem. Coll. Sci. Engin., Kyoto, 2, 394 (1909-1910) (p. 17).

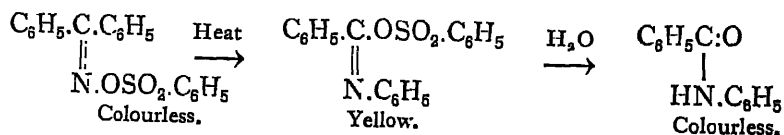
3 Lieb. Ann., 175, 320, 323 (1875).

benzhydroxamic acid and its salt, although they do not contain the negative acid residue; in this case, therefore, the decomposition can not be accounted for as the result of the Beckmann rearrangement of the usual type, as we assume, so it may be founded upon some other scheme of reaction. The authors then put forward an explanation by applying Hantzsch's view¹ on the rearrangement of benzhydroxamic acid, that is to say, that benzhydroxamic acid forms an anhydride which intramolecularly undergoes rearrangement:



Now, it has become evident that rearrangement does not take place in an aqueous solution of the salt of benzhydroxamic acid, as has already been stated, because the formation of an anhydride is not possible on account of the presence of water. Nevertheless, in an aqueous solution of the salt of hydroxamic acid acyl ester (dihydroxamic acid), in fact rearrangement takes place, as is indicated by the production of disubstituted urea as has been stated, although the formation of hydroxamic acid or its salt is possible by hydrolysis, but their rearrangement should not take place as their dehydration can not be effected in presence of water; in such a case, therefore, the migration of a negative acid residue must be brought about as the primary cause of rearrangement.

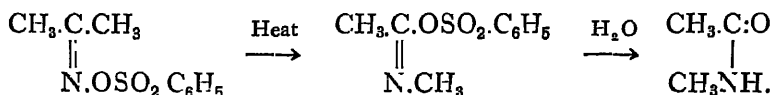
Recently an interesting observation was made by one of us (M.K.), Nakaseko and Matsunami in our laboratory with regard to the rearrangement of benzenesulphonyl ester of diphenylketoxime, viz, that the ester prepared from the sodium salt of diphenylketoxime by the action of benzenesulphonyl chloride at a low temperature, which is a colourless crystalline substance, changes to a yellow coloured compound gradually on standing by itself, but instantaneously with explosive violence accompanied by a hissing sound by heating; the yellow compound being unstable, changes readily to benzanilide by treating with water. The course of reaction shall be represented by the following scheme:



1 Ber. D. Chem. Ges., 27, 1255 (1894).

in which the formula of the intermediate product points out the presence of a characteristic chromophoric group, $>\text{C}:\text{N}.\text{C}_6\text{H}_5$.¹

Also, Hermann Weg² has shown that benzenesulphonyl ester of acetoxime, $(\text{CH}_3)_2\text{C}:\text{N}.\text{OSO}_2\text{C}_6\text{H}_5$, decomposes explosively with a hissing noise by heating, but nothing is said about the production of a substituted acid amide. Yura, however, found as the result of an experiment suggested by one of us (M.K.) that the principal decomposition product consists of a methylamine-producing compound which may be regarded as methylacetamide, as it yields methylamine by treating with alkali; thus the reaction shall be represented as follows:



He further experimented with the benzoyl and acetyl esters of acetoxime, and observed, likewise, the production of methylamine from the decomposition product, although not so much as in the case of benzenesulphonyl ester.

Jones³ has recently mentioned in his article that the potassium salt of the benzoyl ester of phenylacethydroxamic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{C}(\text{OK}):\text{N}.\text{OCO}.\text{C}_6\text{H}_5$, dried upon a porous support, suddenly decomposes in the course of a few minutes, accompanied by a hissing sound and a dense cloud of benzylisocyanate, and also that in a similar manner, certain other salts of hydroxamic acids, when heated to a temperature considerably above room temperature, decompose explosively. Thiele and Pickard⁴ already noticed that acetyl and benzoyl esters of hydroxamic acid yield potassium salts which explodes by heating. So, the authors believe that such a decomposition is due to the spontaneous rearrangement analogous to that of the ketoxime esters as above stated.

Now such an explosion with a hissing sound, which occurs suddenly in the decomposition of the different compounds of the oxime type may be regarded as a particular phenomenon accompanying the spontaneous Beckmann rearrangement, viz., the self-migration of an acid residue and a hydrocarbon radical.

1 Mem. Coll. Sci. Engin., Kyoto, 2, 366 (1909-1910).

2 Ber. D. Chem. Ges., 24, 3537 (1891).

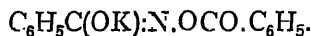
3 Amer. Chem. J., 48, 8 (1912).

4 Liebig Ann., 309, 190 (1899).

The investigation relating to the rearrangement of benzenesulphonyl and other acyl esters of different ketoximes is now in progress; the details of the result will be communicated in a near future.

EXPERIMENTAL.

1. *Potassium Dibenzhydroxamate*,



Five grams of dibenzhydroxamic acid prepared according to the method by Lossen¹, was suspended in water, and a solution of potassium hydroxide was carefully added until it dissolves, and then the solution was subjected to distillation by passing a current of steam. Adding a drop of a solution of bleaching powder to a small portion of the distillate, there was observed the characteristic colour-reaction of aniline. The principal portion of the distillate was extracted with ether, and the liquid substance left on evaporation of ether was confirmed to be aniline by changing it to the double salt of its hydrochloride with platinum chloride.

The similar experiment was conducted by using an aqueous solution of the neutral potassium salt of dibenzhydroxamic acid, prepared as usual, by treating the acid with alcoholic potash. The result was found to be same as above described.

2. *Potassium Benzhydroxamate*, $\text{C}_6\text{H}_5\text{C(OK):N.OH}$.

The experiment exactly similar to that above stated was performed with the potassium salt of benzhydroxamic acid from the acid prepared according to the statement given by Lossen², but not a trace of aniline was found to be formed, not giving the characteristic delicate colour-reaction of aniline.

3. *Ethylbenzhydroxamic acids*, $\text{C}_6\text{H}_5\text{C(OC}_2\text{H}_5\text{):N.OH}$.

Each of both geometrical isomers of ethylbenzhydroxamic acid (the syn ester melts at 53° and the anti at 67°)³ was heated at the

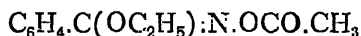
1 Lieb. Ann., 161, 347 (1872).

2 Ibid.

3 Ber. D. Chem. Ges., 17, 1587 (1884); 25, 37-39 (1892); Lieb. Ann., 205, 279 (1880).

temperature of 70-80° for twelve hours over a water bath. The product from each was subjected to steam distillation in an alkaline solution, but the distillate gave no colour-reaction of aniline at all. Hence, it is concluded that the Beckmann rearrangement would not take place in the potassium salt and both esters of benzhydroxamic acid.

4. *Ethylbenzhydroximic Acetates,*



Syn and anti acetates of ethylbenzhydroximic acid prepared according to Werner's description¹ melt at 38-39° and 57° respectively.

Three grams of the syn acetate were heated at the temperature of 67-70° for twelve hours, and the product was subjected to steam distillation in an alkaline solution. The production of a small quantity of aniline was confirmed in the distillate by the colour-reaction with a bleaching powder solution.

5. *Action of Hydrochloric Acid upon
Ethylbenzhydroximic Acetates.*

Three grams of ethylsynbenzhydroximic acetate dissolved in 30 c.c. of chloroform saturated with hydrochloric acid were heated in a sealed tube at 100-102° for twelve hours. When the tube was opened, the escapement of ethyl chloride was noticed; the contents of the tube were poured into a glass vessel where chloroform and hydrochloric acid were driven out by evaporation, a reddish brown liquid being left as a residue. From this liquid, phenylurethane and acetyl benzhydroxamic acid were isolated. In order to conduct the separation of those compounds, the reaction products were first treated with ether and then with benzene, as phenylurethane and acetyl phenylurethane are soluble in ether while acetyl benzhydroxamic acid not in ether but in benzene and water. Each of those substances was identified by its melting point and other characteristic behaviours.

1 Ber. D. Chem. Ges., 25, 40-41 (1892).

On the Beckmann Rearrangement. IV.

Acyl Derivatives of the Substituted Imido-Acids.

By

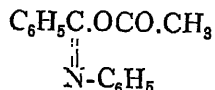
Mitsuru Kuhara and Kanoichiro Suitsu.

(Received July 6, 1914.)

It is almost evident that the intermediate formation of the acyl derivatives of the substituted imido-acids is a necessary condition of the Beckmann rearrangement of the ketoximes by the acid chlorides, acids, etc., as has been often mentioned in the previous articles¹ by one of us (M.K.) and his collaborators. Expecting that the isolation and synthesis of such compounds, if possible, may throw some more light upon the nature of the Beckmann rearrangement, an investigation for such a direction has been attempted as a subject of particular interest.

Wheeler and Johnson² have explained the formation of diacylanilides by the action of acyl chlorides upon the silver salts of acylanilides. Mumm³ has synthesized several acylbenzanilides by shaking an ethereal solution of phenylbenzimidochloride (benzanilidimide chloride)⁴ together with the aqueous solutions of the sodium salts of several organic acids. The actual isolation, however, of the acyl derivatives of the substituted imido-acids (pseudoamides), which would seem to be the intermediate products of the reactions, has not been effected.

Carrying out an experiment suggested by one of us (M.K.), Kodama has succeeded to isolate a compound which may be considered to be formed from diphenylketoxime through the Beckmann rearrangement by acetyl chloride, and must possess the constitution corresponding to phenylbenzimidacetate⁵,



1 Mem. Coll. Sci. Engin., Kyoto, 1, 254 (1903-1908) (p. 1); 2, 367 (1909-1910) (p. 11); These Memorials, 1, 1 (1913) (p. 19).

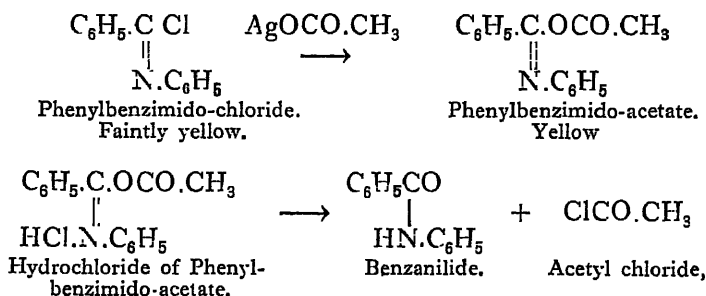
2 Amer. Chem. J., 19, 188 (1897). Refer *ibid.*, 18, 381 (1896).

3 Ber. D. Chem. Ges., 43, 886, 8336 (1910).

4 Lieb. Ann., 184, 97 (1777).

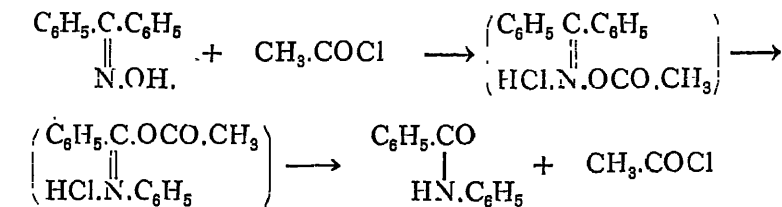
5 Mem. Coll. Sci. Engin., Kyoto, 2, 305 (preliminary communication) (p. 18).

by treating an ethereal solution of phenylbenzimidochloride with silver acetate. The substance is a thick yellow oil of unstable nature, and forms its hydrochloride as a canary yellow precipitate by passing dry hydrochloric acid through its ethereal solution cooled with a freezing mixture, but by the excess of the acid changes to acetylbenzanilide,¹ probably by the secondary reaction. The hydrochloride dissolved in chloroform and heated above 60° yields benzanilide at once. When sodium acetate is used for its preparation instead of silver acetate, the product always consists entirely of acetylbenzanilide. Then, the reactions for the formation of phenylbenzimidacetate and for decomposition of its hydrochloride into benzanilide shall be represented as follows:



And the production of acetylbenzanilide may be the result of the secondary reaction or of the intramolecular rearrangement noticed by Mumm.²

Now the last phase of the Beckmann rearrangement of diphenylketoxime by acetyl chloride is highly probable to be due to the above-mentioned decomposition of the hydrochloride of phenylbenzimidacetate which is assumed to be formed as an intermediate product in the rearrangement of diphenylketoxime acetyl ester formed in reaction, being inferred from its behaviours; so for convenience the whole scheme of the Beckmann rearrangement, as it is assumed, shall be stated again:

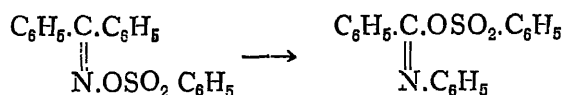


1 Amer. Chem. J., 18, 546 (1896).

2 Loc. cit.

It is, however, not possible to isolate phenylbenzimidio-acetate as an intermediate product from diphenylketoxime acetyl ester by its intramolecular rearrangement, as the latter does not undergo the rearrangement by itself even by the rise of temperature, on account of the weak negative character of the acetic acid residue present, but always the aid of hydrochloric acid is needed for its rearrangement as has been often stated. When hydrochloric acid is present, therefore, phenylbenzimidio-acetate formed would yield its hydrochloride, and its decomposition may progress until the extreme so that its isolation as an intermediate product is not possible.

Nevertheless, diphenylketoxime benzenesulphonyl ester actually undergoes the spontaneous rearrangement without the aid of any reagent, owing to the presence of the strong negative acid residue, with the formation of phenylbenzimidio-benzenesulphonate whose isolation is possible, the scheme of rearrangement being represented here again :



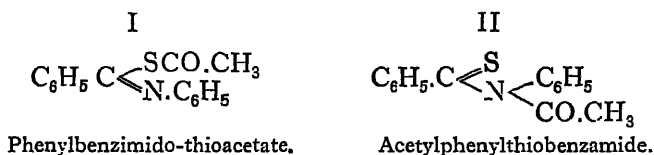
In fact, phenylbenzimidio-benzenesulphonate has been isolated by one of us (M. K.) and Matsunami from diphenylketoxime benzenesulphonyl ester by rearrangement, and an account has been preliminarily communicated to the Memoirs of the College of Science and Engineering¹.

As has been already mentioned, it is not only difficult to isolate phenylbenzimidio-acetate as an intermediate product of the rearrangement of diphenylketoxime by acetyl chloride, but also it is a hard task to prepare it synthetically in a perfectly pure state by the action of metallic acetate upon phenylbenzimidio-chloride without exception, often resulting only in the production of benzanilide and acetylbenzanilide; so we are not able to catch a just right condition for the constant formation of the yellow oil or phenylbenzimidio-acetate. The authors, have, therefore, attempted to synthesize the other esters of the same type by the action of the metallic salts of the other acids upon phenylbenzimidio-chloride, in order to see if the actual isolation of the esters of such a kind as phenylbenzimidio-acetate is possible. For this purpose, at first the synthesis of phenylbenzimidio-thioacetate was carried out, fortunately with success. In the experiment, potassium thioacetate,

1 Mem. Coll. Sci. Engin., Kyoto, 6, 7 (1913) also refer These Memoirs, 1, 7 (1913). (p. 19).

KS.CO.CH_3 , was made to react with phenylbenzimidio-chloride, dissolved in petroleum ether in presence of anhydrous potassium carbonate as the ordinary temperature, by which process the yellow coloration of the solution was at first observed, followed by its gradual change to orange red. On allowing the solution to stand for several days, yellow crystals were found to deposit mixed with some orange red crystals; and two substances were separated by fractional crystallization and each analysed. Both substances possess the same composition corresponding to the empirical formula $\text{C}_{15}\text{H}_{13}\text{NOS}$.

It is now concluded that the yellow compound would be phenylbenzimidio-thioacetate possessing the constitution represented by the formula I, and the orange red substance would be acetylphenylthiobenzamide having the formula II:



interpreting from the facts which will be described hereinafter:

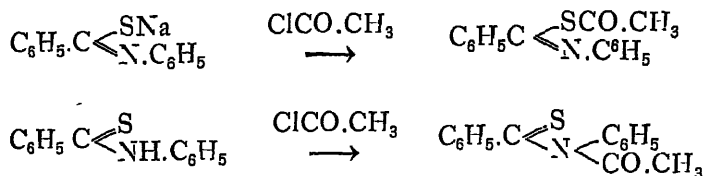
1. When the perfectly pure phenylbenzimidio-chloride is allowed to interact with potassium thioacetate, the yellow compound alone is formed, not a trace of the orange red compound being observed to be formed.

2. The yellow compound changes to the orange red isomer, when comes in contact with phosphorus oxychloride, acetyl chloride, benzoyl chloride, alkali, etc., or when kept in a vessel filled with hydrochloric acid gas. It is then assumed that the yellow compound is the primary reaction-product of phenylbenzimidio-chloride and thioacetate, which may secondarily change to the orange red isomer by the aid of the acid possibly present in the chlorides used or by alkali:

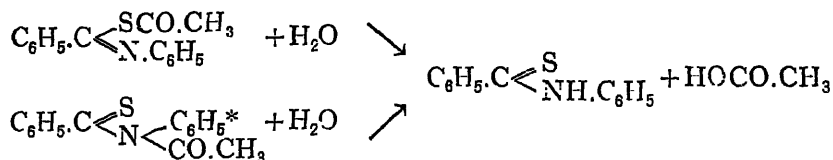
3. The formula I indicates the presence of a chromophoric group, $\text{>C=N.C}_6\text{H}_5$, which is assumed to give rise to the manifestation of yellow colour.¹

4. Acetyl chloride, when react with sodium salt of thiobenzanilide suspended in xylene, yields a considerable amount of the yellow compound, while in a dry etherial solution of thiobenzanilide in presence of anhydrous potassium carbonate it produces the orange red compound; the reactions in both cases should be represented as follows:

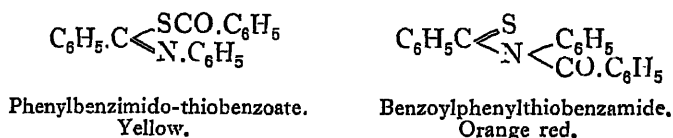
1 Mem. Coll. Sci. Engin., Kyoto, 2, 366 (1909-1910).



5. Subjecting both yellow and orange red compounds to hydrolysis by means of dilute acid or alkali, they are decomposed yielding the same products, that is, thiobenzanilide and acetic acid. Such phenomena of decomposition may be shown by the following scheme:



Continuing experiment further with potassium (or silver) thiobenzoate and phenylbenzimidochloride under the same condition, it has also been noticed that both yellow and orange red compounds are produced as in the other case. Their behaviours are similar with those of the corresponding thio-compounds above mentioned; hence by analogy their respective constitutional formulas should be represented as follows:



In conclusion it may be said that the existence of the esters of the types, $\text{C}_6\text{H}_5\cdot\text{C}(\text{OCOR})\text{:N}\cdot\text{C}_6\text{H}_5$, $\text{RC}(\text{OSO}_2\text{C}_6\text{H}_5)\text{:NR}$ and $\text{C}_6\text{H}_5\cdot\text{C}(\text{SCOR})\text{:N}\cdot\text{C}_6\text{H}_5$ (in which $\text{R}=\text{C}_6\text{H}_5$ or CH_3) is possible, and that the esters corresponding to the first two formulas would be formed as the intermediate products of the Beckmann rearrangement of the respective ketoximes by the respective acid chlorides, inferring from their behavi-

* In the mixed diacylanilides, the lower acyl group is removed according to Wheeler, Smith and Warren's view.—*Amer. Chem. J.*, 19, 758, (1897).

ours as well as from their actual isolation in the course of rearrangement. Especially, the investigation with regard to the rearrangement of benzenesulphonyl esters of ketoximes is now going on in our laboratory.

EXPERIMENTAL PART.

I. *Action of Silver Acetate upon Phenylbenzimidochloride.*

A slight excess of finely powdered anhydrous silver acetate over an equivalent quantity was added by small quantities to a well cooled ethereal solution of phenylbenzimidochloride (benzanilidimide chloride) prepared according to Wallach's statement,¹ with constant and vigorous shaking of the mixture. At the beginning of reaction the white silver salt turned yellow on its surface, but the liquor soon got yellow, gradually increasing in depth, as the yellow substance formed passes into solution. The ethereal solution was then filtered, and ether removed by evaporation quickly passing a current of dry air. In the course of evaporation, there separated out at first some platy crystals which were confirmed to be benzanilide by its characteristic properties, soon followed by the deposition of colourless needle-shaped crystals and finally there remained a thick yellow oil. The needle-shaped crystals purified by repeated recrystallization from petroleum ether and also from dilute alcohol were found to melt at 63.5° and to possess all the properties of acetylbenzanilide already obtained by Wheeler and McFarland². The oil was then treated with petroleum ether for its purification, and the solution, was allowed to evaporate by passing a current of dry air. Its analysis has not been conducted, as the substance is very difficult to be obtained in a perfectly pure state on account of its changeable character, yet the substance should undoubtedly be phenylbenzimidacetate, $C_6H_5.C(OCO.CH_3):N.C_6H_5$, being inferred from its behaviours.

By passing a current of dry hydrochloric acid through an ethereal solution of the oil cooled with a freezing mixture*, its hydrochloride separated out as a canary yellow precipitate which can be reconverted into the original substance by means of anhydrous potassium carbonate. The hydrochloride, when exposed to moist air, soon changed reddish brown, with the formation of benzanilide, aniline and acetic

1 Lieb. Ann., 184, 79 (1877).

2 Amer. Chem. J., 18, 546 (1896).

acid as its decomposition products. Heating the hydrochloride dissolved in dry chloroform in a sealed tube above 60° for about half an hour, it was found to be transformed into benzanilide. The oil itself alone dissolved in chloroform or benzene, when heated in a sealed tube at $160-170^{\circ}$ for about two hours showed no perceptible change. It readily decomposes by acid and alkali splitting up into acetic acid (or its salt) and benzanilide.

2. *Action of Sodium Acetate and of Silver Benzoate upon Phenylbenzimidochloride.*

Gently warming an ethereal solution of phenylbenzimidochloride mixed with some powdered anhydrous sodium acetate, and then evaporating the solution, the residue was extracted with petroleum ether, by which process acetylbenzanilide¹ was isolated without the intermediate formation of the yellow isomer.

By the action of silver benzoate upon phenylbenzimidochloride dissolved in ether, a yellow oil and needle-shaped crystals were isolated besides benzanilide and some benzoic acid. The needle-shaped crystals were found to be dibenzoylanilide², as it possesses the melting point of 155° (Losanitsch) and all its characteristic properties. The yellow oil should be phenylbenzimidobenzoate, since its formation and decomposition are wholly analogous with those of the acetyl ester obtained from silver acetate and phenylbenzimidochloride.

The formation of acetyl- and dibenzoylanilides in those cases above described may be due to the rearrangement noticed by Mumm.

3. *Action of Potassium Thioacetate upon Phenylbenzimidochloride.*

Finely powdered anhydrous potassium thioacetate was added to a dry petroleum ether solution of phenylbenzimidochloride previously mixed with some anhydrous potassium carbonate in order to avoid the action of acid which is possible to be present, and the mixture was constantly shaken for a while at the ordinary temperature. At the beginning of reaction, the surface of potassium thioacetate was covered

¹ Loc. cit.

² Refer Beilstein II, 1171. Ber. D. Chem. Ges., 43, 886 (1910).

with a yellow coating, but the solution soon changed pink, followed by the gradual increase of the depth of colour. On allowing the mixture to stand for a few days with occasional shaking, the yellow coloured phenylbenzimidio-thioacetate was found to deposit, mixed with the orange red crystals of acetylphenylbenzamide. The mixture was filtered, and the residue treated with warm petroleum ether and the solution concentrated by distillation under a diminished pressure. Letting the concentrated solution stand for a while there separated out a mass of granular orange red crystals. The substance purified by recrystallization from dry petroleum ether, consists of deep orange red coloured needles, and melts at $78.5-79.5^{\circ}$. It is soluble in common organic solvents with dark orange red colouration. Its analysis gave the following values for sulphur:

I.	0.2384	grm.	substance	gave	0.222	grm.	BaSO ₄ .
II.	0.2576	„	„	„	0.237	„	„
III.	0.1860	„	„	„	0.171	„	„

	Calculated for		Found	
	$C_6H_5.C(N.C_6H_5.CO.CH_3):S$	I	II	III
Sulphur	12.57	12.75	12.64	12.63

Warming with dilute acid or alkali, it is readily transformed into thio-benzanilide melting at $97.5-98.5^{\circ}$.

The last residue left after extracting with petroleum ether was treated with chloroform, and the solution thus obtained was allowed to evaporate by passing a current of dry air; the residue consisting of phenylbenzimidio-thioacetate was repeatedly washed with cold absolute alcohol and then dissolved in a mixture of chloroform and ether. On allowing the solution to stand for a while there deposited a lot of monoclinic amber-yellow coloured crystals.

The analysis of the substance gave the following values for sulphur:

I.	0.1530	grm.	substance	gave	0.1406	grm.	BaSO ₄ .
II.	0.2402	„	„	„	0.2172	„	„

	Calculated for		Found
	$C_6H_5.C(SCO.CH_3):N.C_6H_5$	I	II
Sulphur	12.57	12.62	12.41

Phenylbenzimidio-thioacetate is of rather stable nature, difficultly soluble in alcohol, ether, petroleum ether, benzene and acetone, but readily in chloroform. By boiling with alcohol or warming with acid or alkali it is transformed into thiobenzanilide with more difficulty than its isomer, acetylphenylthiobenzamide. The yellow crystals of phenylbenzimidio-thioacetate, when heated, melt to a deep orange red liquid, which solidifies to the original yellow substance when cooled. The substance being brought in contact with phosphorus oxychloride, acetyl chloride, benzoyl chloride or caustic alkali, or being kept under a desiccator filled with dry hydrochloric acid gas, is transformed into the orange red isomer. In the latter case, the reaction progresses until the extreme so as to produce thiobenzanilide, when it is allowed to stand for several days. On boiling the substance with water no perceptible change is observed to take place. Purer the phenylbenzimidio-chloride used is, the less acetylphenylthiobenzamide is produced; thus when potassium thioacetate is allowed to react with the well purified phenylbenzimidio-chloride, phenylbenzimidio-thioacetate alone is observed to be formed without the addition of potassium carbonate. From such a relation, it is almost evident that phenylbenzimidio-thioacetate formed as a primary product of reaction would change to isomeric acetylphenylthiobenzamide by the action of acid, which is probable to be mixed with the impure phenylbenzimidio-chloride, being derived from phosphorus oxychloride, acid chlorides, etc. used.

4. *Action of Acetyl Chloride upon Thiobenzanilide and upon its Sodium Salt.*

On adding an ethereal solution of an equivalent quantity of the purified acetyl chloride to an ethereal solution of thiobenzanilide in presence of anhydrous potassium carbonate, the solution was soon observed to alter deep orange red under the evolution of carbon dioxide. Evaporating the solution by passing a current of dry air through it, there was left an orange red substance; and from the petroleum ether solution of the latter the orange red coloured crystals separated out and were found to possess all the properties of acetylphenylthiobenzamide, $C_6H_5.C.(N.C_6H_5.COCH_3):S$.

I gram of metallic sodium was added to 9 grams of thiobenzanilide dissolved in 100 grams of dry xylene, and the mixture was heated for 15 hours in a flask provided with an inverted condenser over an oil

bath at the temperature of 110-120°. When the reaction ended, the whole contents were cooled, and 20 c.c. of 1 molar solution of acetyl chloride in xylene were gradually added from a burette. At first there deposited some phenylbenzimidio-thioacetate alone, then the solution getting orange red. Driving off xylene from the mother liquor by continually passing a current of dry air for several days, phenylbenzimidio-thioacetate was left as a residue together with some orange red isomer and colourless crystals. The whole residue, by treating with cold absolute alcohol, left the yellow crystals of phenylbenzimidio-thioacetate undissolved. The solubility, crystalline form and chemical properties of the substance show that it is identical with phenylbenzimidio-thioacetate, $C_6H_5.C.(SCO.CH_3):N.C_6H_5$, obtained from phenylbenzimidide and sodium thioacetate.

5. *Action of Potassium Thiobenzoate upon Phenylbenzimidio-chloride.*

By the action of potassium thiobenzoate upon phenylbenzimidio-chloride dissolved in dry petroleum ether in presence of anhydrous potassium carbonate at the ordinary temperature, there deposited some yellow compound at first, followed by the gradual increase of the depth of red colour of the mother liquor. Allowing the mixture to stand for a month, a lot of yellow compound was found to crystallize out together with some orange crystals. Two compounds were separated by the similar treatment as in the case of two analogous acetyl derivatives of thiobenzanilide mentioned before.

The orange red compound is soluble in common organic solvents, melts at 110-111° and decomposes into thiobenzanilide and benzoic acid by heating with dilute acid or alkali. The analysis of the substance gave the following value for sulphur:

0.2371 grm. substance gave 0.1684 grm. $BaSO_4$.

Calculated for C ₆ H ₅ .C(SCO.C ₆ H ₅).N.C ₆ H ₅		Found
Sulphur	10.11	
		9.76

Accordingly the orange red compound would be no doubt benzoyl-phenylthiobenzamide, and as the yellow one is similar to phenylbenzimidio-thioacetate in all respects, so it should be phenylbenzimidio-thiobenzoate, $C_6H_5.C.(SCO.C_6H_5):N.C_6H_5$.

On the Beckmann Rearrangement. V.

Rearrangement of Diphenylketoxime Benzenesulphonyl Ester and Synthesis of Phenylbenzimidobenzenesulphonate.

By

Mitsuru Kuhara,

Kaoru Matsumiya and Naohiko Matsunami.

(Received November 30, 1914.)

As has already been mentioned in the previous articles¹ by one of us (M.K.) and his collaborators, diphenylketoxime benzenesulphonyl ester actually undergoes the spontaneous molecular rearrangement, whose primary cause may be ascribed to the dissociation of the benzenesulphonic acid residue of strongly negative character as we assume, with the consequent formation of phenylbenzimidobenzenesulphonate, thus giving a possible explanation as regards the mechanism of the Beckmann rearrangement.

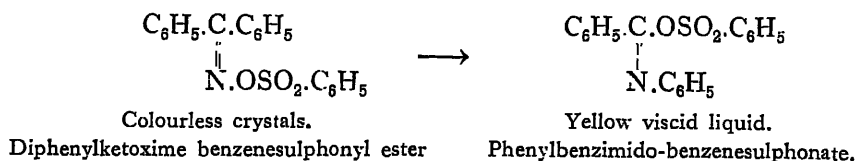
Diphenylketoxime benzenesulphonyl ester used in the present work was prepared from the sodium salt of diphenylketoxime² by the action of benzenesulphonyl chloride³ at the ordinary temperature. It is a colourless crystalline substance, whose nature was confirmed by saponification with alkali by which process it splits up readily into its constituents, i.e., diphenylketoxime and benzenesulphonic acid. As a matter of fact, the ester changes by the molecular rearrangement to a yellow viscid liquid, which is no doubt phenylbenzimidobenzenesulphonate, slowly on being allowed to stand by itself in a solid state in a chloroform solution, or by exposing its powder to the ultra-violet rays, but instantaneously with explosive violence accompanied by a hissing noise on heating above its melting point 62°; thus the change should be as follows, as has already been shown⁴:

1 Mem. Coll. Sci. Engin., Kyoto, 2, 385 (1910), (p. 11); These Memoirs, 1, 1 (1914), (p. 19); 1, 25 (1914), (p. 28).

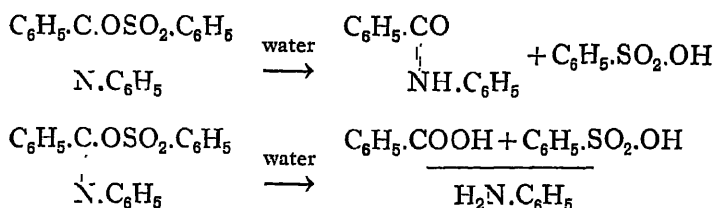
2 Ber. D. Chem. Ges., 17, 812 (1884).

3 Lieb. Ann., 87, 299 (1853); Z. f. Chem., 1866, 103.

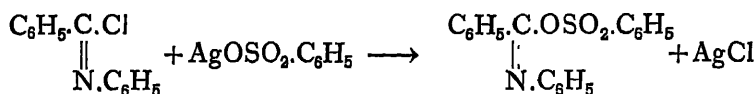
4 *Loc. cit.*



Phenylbenzimidobenzenesulphonate which is of unstable character, gradually changes to benzanilide and benzenesulphonic acid by moisture on being left in open air, but very readily by treating with water, sometimes still further decomposition taking place with the production of aniline, benzoic acid and benzenesulphonic acid, when is kept in a moist chloroform solution; thus the reactions should be as follows:



Phenylbenzimidobenzenesulphonate was then synthesized from phenylbenzimidochloride¹ by the action of silver benzenesulphonate². In this experiment, phenylbenzimidochloride prepared as purely as possible with all necessary precautions, and dissolved in petroleum ether was allowed to react with silver benzenesulphonate under constant and vigorous shaking, and then the solid separated from petroleum ether by filtration was treated with chloroform. Evaporating chloroform by passing a rapid current of dry air through the solution, there was left a yellow viscid liquid, some benzanilide separated from the concentrated solution having been removed by filtration through cotton wool. The substance, thus prepared by synthesis corresponds to phenylbenzimidobenzenesulphonate, inferring its composition from the analytical results; hence the reactions should be represented as follows:



The substance possesses the same behaviours as the benzenesulphonate formed by the rearrangement of diphenylketoxime benzenesulphonyl

1 Lieb. Ann., 184, 79 (1877); Ber. D. Chem. Ges., 43, 892 (1910).

2 Lieb. Ann., 223, 244 (1884).

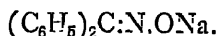
ester, thus readily decomposing into benzanilide and benzenesulphonic acid, and also into benzoic acid, benzenesulphonic acid and aniline by the action of water.

Further, the absorption spectra of the two preparations of phenylbenzimidobenzenesulphonate from two different sources, that is, one formed by rearrangement and the other prepared by synthesis, were examined under the same condition. On comparing their absorption curves, as will be seen in the experimental part, it has been found that they almost agree to each other.

Now from the experimental results so far obtained a conclusion is drawn that phenylbenzimidobenzenesulphonate formed from diphenylketoxime benzenesulphonyl ester is identical with that obtained by synthesis from phenylbenzimidochloride and silver benzenesulphonate. It is, therefore, quite evident that diphenylketoxime benzenesulphonyl ester undergoes the molecular rearrangement spontaneously, owing to the presence of the benzenesulphonic acid residue of strongly negative character without the aid of any reagent, more readily by the mere elevation of temperature; consequently the production of the acyl derivative of the substituted imido-acid from the ketoxime acyl ester must be a necessary condition of the Beckmann rearrangement.

EXPERIMENTAL PART.

I. Sodium Salt of Diphenylketoxime.



Since the method of the preparation of the sodium salt of diphenylketoxime proposed by Spiegler¹ gives a very poor yield, the authors have suggested the other method which is very simple and satisfactory. It consists in adding thin slices of metallic sodium to the solution of diphenylketoxime in absolute ether, by which treatment there was noticed a brisk evolution of hydrogen and the deposition of the sodium salt of diphenylketoxime in the form of a light white powder. The latter was then separated from the unchanged metallic sodium left in ether by decantation after shaking the whole mixture violently, and then repeatedly washed with ether until not a trace of diphenylketoxime unchanged is detected in washings. The salt thus prepared was dried in a desiccator and analysed.

1 Ber. D. Chem. Ges., 17, 812 (1884).

0.1594 grm. substance gave 0.08 grm. Na_2SO_4 .

	Calc. for $(\text{C}_6\text{H}_5)_2\text{C:N.ONa}$	Found
Sodium	10.47	10.56

As a by-product of the reaction there was found a small quantity of aminodiphenylmethane, $(\text{C}_6\text{H}_5)_2\text{CH.NH}_2$, whose formation is undoubtedly due to the reduction of diphenylketoxime by hydrogen liberated.

2. Diphenylketoxime Benzenesulphonyl Ester.



Equivalent quantities of the sodium salt of diphenylketoxime and benzenesulphonyl chloride¹ mixed in absolute ether were allowed to react to each other for several hours under vigorous shaking. The ethereal solution, then separated by filtration from sodium chloride formed in the reaction, was made to evaporate by passing a current of dry air in order to avoid the rise of temperature, by which process colourless crystals of diphenylketoxime benzenesulphonyl ester were deposited. Repeating its recrystallization from ether, it was obtained in pure state. The ester was analysed, and gave the following value for sulphur.

0.186 grm. substance gave 0.126 grm. BaSO_4 .

	Calc. for $(\text{C}_6\text{H}_5)_2\text{C:N.OSO}_2.\text{C}_6\text{H}_5$.	Found
Sulphur	9.51	9.30

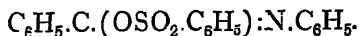
The substance is soluble in alcohol, benzene and chloroform, and melts at 62° with some change.

In order to confirm the nature of the ester, it was treated with alcoholic potash by the action of which it was found to decompose into diphenylketoxime and benzenesulphonic acid. The former was identified by its melting point and the latter by the analysis of its barium salt which gave the following value for barium.

0.109 grm. of the anhydrous salt gave 0.555 grm. BaSO_4 .

	Calc. for $(\text{C}_6\text{H}_5 \text{ SO}_2\text{O})_2\text{Ba}$	Found
Barium	30.42	30.13

¹ Lieb. Ann., 87, 299 (1853).

3. *Phenylbenzimidobenzenesulphonate.*

By heating the crystals of diphenylketoxime-benzenesulphonyl ester above its melting point, they change instantaneously to a yellow viscid liquid with an explosive violence accompanied by a hissing sound. Such a change is, however, gradually effected on allowing the crystals to stand under a desiccator for a long while, or by dissolving them in chloroform, the solution getting slowly yellow. It was also observed that the ester in the form of fine powder, when introduced between a pair of thin quartz plates and exposed to the ultra-violet rays from a mercury lamp, changes yellow on its surface in an hour. The analysis of the substance gave the following values for sulphur.

I.	0.1140	gram.	substance	gave	0.0762	gram.	BaSO ₄ .
II.	0.1552	„	„	„	0.1214	„	„
III.	0.1062	„	„	„	0.0741	„	„
			Calc. for			Found	
			$\text{C}_6\text{H}_5\cdot\text{C}(\text{OSO}_2\cdot\text{C}_6\text{H}_5):\text{N}\cdot\text{C}_6\text{H}_5$	I	II	III	Mean
Sulphur			9.51	9.17	10.07	9.30	9.52

The yellow viscid liquid is without doubt phenylbenzimidobenzenesulphonate formed by the molecular rearrangement of diphenylketoxime benzenesulphonyl ester, as it readily decomposes into benzanilide and benzenesulphonic acid by treating with water. Benzanilide was confirmed by its melting point and other properties, and benzenesulphonic acid by the analysis of its barium salt.

0.2 gram. of the anhydrous barium salt gave 0.108 gram. BaSO₄.

	Calc. for $(\text{C}_6\text{H}_5\cdot\text{SO}_2\text{O})_2\text{Ba}$	Found
Barium	30.42	31.79

The substance, when exposed to air, slowly decomposes into benzanilide and benzenesulphonic acid owing to its unstable nature in presence of moisture; it is, however, pretty stable in vacuum. It is soluble in alcohol, chloroform and acetone. By keeping its solution in moist chloroform for a while, some colourless silky needle-shaped crystals were found to separate out. They melt above 200° with decomposition, and soluble in water, alcohol and acetone. They decompose into aniline and benzenesulphonic acid by treating with a solution of alkali;

aniline isolated by extracting with ether was confirmed by its colour-reaction with a bleaching powder solution, and benzenesulphonic acid contained in the alkaline aqueous part by the analysis of its barium salt.

0.115 grm. of the anhydrous barium salt gave 0.0593 grm. BaSO_4 .

	Calc. for $(\text{C}_6\text{H}_5\cdot\text{SO}_2\text{O})_2\text{Ba}$	Found
Barium	30.42	30.60

The mother liquor consisting of the chloroform solution was evaporated, and from the residue benzoic acid was isolated and confirmed by its melting point and other characteristic properties. The substance which consists of silky needles is, therefore, the aniline salt of benzenesulphonic acid; and on comparing it with the salt prepared according to Gericke¹ from aniline and benzenesulphonic acid, both were found to be identical. Hence phenylbenzimidobenzenesulphonate in the chloroform solution decomposes, in fact, into aniline benzenesulphonic acid and benzoic acid through the action of moisture contained in it.

4. *Synthesis of Phenylbenzimidobenzenesulphonate.*

Phenylbenzimidobenzenesulphonate was synthesized from phenylbenzimidochloride and silver benzenesulphonate, and the process will be described below. Phenylbenzimidochloride (benzanilidimide chloride) was prepared according to the method proposed by Wallach² and purified by the process suggested by Mumm³ with all possible precautions, and the anhydrous silver benzenesulphonate was obtained by Hübner's method.⁴ Phenylbenzimidochloride, thus prepared, was dissolved in dry petroleum ether, and anhydrous silver benzenesulphonate added in some excess over an equivalent quantity. With the constant and vigorous shaking of the mixture, silver benzenesulphonate gradually changed yellow on its surface, and finally a yellow substance deposited in the wall of a vessel. After removing petroleum ether by decantation, the yellow substance was extracted by treating the residue with chloroform which produced a deeply yellow-coloured solution. Evaporating chloroform by passing a current of dry air through the chloroform solution well excluded from mois-

1 Lieb. Ann., 100, 217 (1857).

2 Ibid., 184, 79 (1877).

3 Ber. D. Chem. Ges., 43, 892 (1910).

4 Lieb. Ann., 225, 244 (1884).

ture, there was left a yellow viscid liquid, mixed with some colourless crystals. The liquid was then separated from the crystals by filtering through cotton wool with the aid of a suction pump. The crystals were identified as benzanilide by its melting point and all other properties. In order to remove the trace of chloroform admixed in the viscid liquid, the latter was left in a desiccator for several hours under constant exhaustion, until no evolution of the bubbles of chloroform was noticed. The substance was analysed and gave the following values for sulphur.

- I. 0.5749 grm. substance gave 0.3835 grm. BaSO_4 .
 II. 0.6092 „ „ „ 0.4522 „ „ .

	Calc. for $\text{C}_6\text{H}_5\cdot\text{C}(\text{OSO}_2\cdot\text{C}_6\text{H}_5):\text{N}\cdot\text{C}_6\text{H}_5$	Found		
		I	II	Mean
Sulphur	9.51	9.19	10.22	9.71

The substance is soluble in alcohol, chloroform and acetone, but difficultly in ether and petroleum ether. By adding water to its solution in acetone, there was found to separate out a flocky precipitate which, when recrystallized from alcohol, melted at 161° , thus proving to be benzanilide. From the filtrate benzenesulphonic acid was isolated as its barium salt by adding some baryta water and removing the excess of barium by means of carbon dioxide. The barium salt recrystallized from water was analysed.

0.425 grm. of the salt gave 0.213 grm. BaSO_4 .

	Calc. for $\text{Ba}(\text{C}_6\text{H}_5\cdot\text{SO}_2\text{O})_2\frac{1}{2}\text{H}_2\text{O}$	Found
Barium	29.83	29.49

The substance dissolved in moist chloroform was also noticed to deposit some colourless silky crystals of the aniline salt of benzenesulphonic acid whose formation must be due to the decomposition of phenylbenzimidobenzene-sulphonate into aniline, benzoic acid and benzenesulphonic acid through the action of moisture contained in chloroform, since by treating the crystals with aqueous alkali they yield aniline and benzenesulphonic acid. The former was confirmed by its colour reaction with a bleaching powder solution and the latter by the production of its barium salt.

0.2381 grm. of the crystals gave 0.2306 grm. BaSO_4 by analysis.

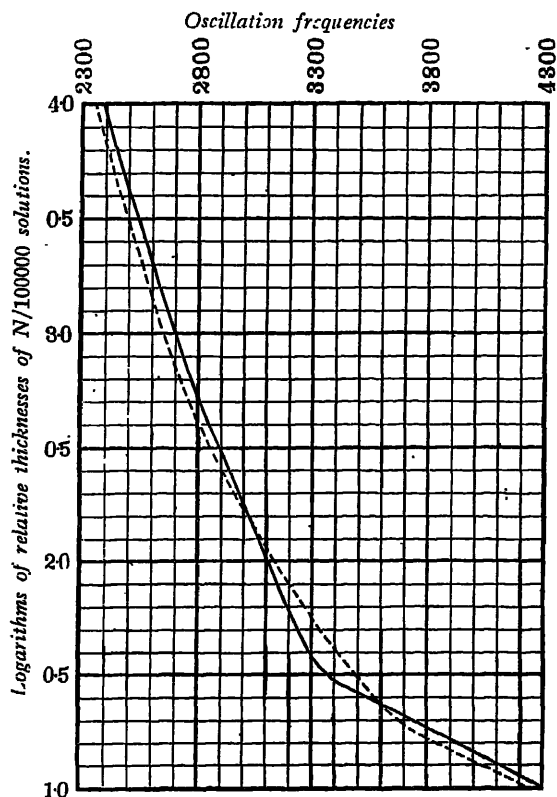
	Calc. for $\text{C}_6\text{H}_5\text{SO}_2\text{O.NH}_3.\text{C}_6\text{H}_5$	Found
Sulphur	12.78	13.30

Aniline benzenesulphonate, thus formed, is identical with that prepared according to Gericke's method.¹

As has been shown so far, phenylbenzimidobenzene sulphonate prepared by synthesis shows no difference in all of its properties in comparison with that formed by the molecular rearrangement of diphenylketoxime benzenesulphonyl ester, hence they should be identical.

5. Absorption Spectra of the two Preparations of Phenylbenzimidobenzene sulphonate.

For the further confirmation of identity of the two preparations of phenylbenzimidobenzene sulphonate, spectrographic experiments were



¹ *Loc. cit.*

conducted according to the well known method by Hartley.¹ For this purpose, their solutions were prepared in absolute alcohol and a Hilger quartz spectrograph was employed with an iron arc as the source of light. An observation was repeated in each case for the different thicknesses of the liquids of several different dilutions with the use of Baly's adjustable cell,² and the absorption curves were plotted with the oscillation frequencies and the relative thicknesses of liquids in terms of the dilution of N/100000. On comparing the curves showing the absorption spectra of the two preparations from the different sources, as represented in the figure, they almost agree to each other, so that they may be concluded to be identical. Thus the full line curve represents the absorption spectra of phenylbenzimidobenzenesulphonate formed by the rearrangement of diphenylketoxime benzenesulphonyl ester and the dash line curve that of the same substance prepared by synthesis from phenylbenzimidochloride and silver benzenesulphonate.

1 J. Chem. Soc., 47, 685 (1885).

2 Ibid., 85, 1039 (1904).

On the Beckmann Rearrangement. VI.

The Rate of Rearrangement of Methylphenylketoxime by the Different Acid Chlorides, the Spontaneous Rearrangement of its Benzenesulphonyl Ester and the Synthesis of Phenylacetimido - benzenesulphonate.

By

Mitsuru Kuhara and Hikohei Watanabe.

(Received April 20, 1916.)

It has already been established by the previous works by one of us (M.K.) and his co-workers¹ that the influence of the different acid chlorides upon the rate of rearrangement of diphenylketoxime would apparently stand in harmony with the degree of acidity² of the acid from which a chloride has been derived, in other words, with the strength of the negative character of the acid residue coupled in the oxime ester which may be formed by an acid chloride, and also that the diphenylketoxime acyl ester containing a strongly negative acid residue, such as diphenylketoxime benzenesulphonyl ester, undergoes of itself the rearrangement without the aid of any reagent, simply at the elevation of temperature, its primary cause being likely due to the dissociation of the benzenesulphonic acid residue of the strongly negative character as we assume, with the subsequent formation of phenylbenzimidobenzene-sulphonate. Such a rearrangement has further been confirmed by the synthesis of phenylbenzimidobenzene-sulphonate which was found to be identical with that actually formed by rearrangement.³

The authors have now attempted to extend the analogous experiments toward a ketoxime of the other class such as methylphenylketoxime (acetophenoxime) anticipating that all the reactions may

1 Mem. Coll. Sci. Engin., Kyoto, 2, 337 (1909-1910), (p. 11); These Memoirs, 1, 106 (1914), (p. 38).

2 Zs. physik. Chem., 1, 73 (1887); J. prak. Chem., 28, 493 (1843).

3 These Memoirs, 1, 106 (1914), (p. 38).

progress in the analogous manner as in the case of diphenylketoxime, and an expectation with regard to such a point of view has been realized.

1. *The Influence of the Different Acid Chlorides.*

For studying the influence of the different acid chlorides upon the rearrangement of methylphenylketoxime, acetyl, monochloroacetyl, benzoyl and benzenesulphonyl chlorides were taken. In every case, an acid chloride and methylphenylketoxime were allowed to react to each other in molecular proportions, each substance having been dissolved in chloroform so as to make $\frac{1}{2}$ molar solution at a definite temperature. Each of both solutions was taken in 5 cc., and two were mixed together and heated at 100° in a sealed tube for a certain period of time. Acetanilide formed was then isolated with a proximate accuracy from the contents of the tube with possible precautions, and its quantity determined. The following table shows the relative quantities of acetanilide formed by rearrangement from methylphenylketoxime by the different acid chlorides.

Time (hours).	% Acetanilide formed,			
	by acetyl chloride.	by benzoyl chloride.	by monochloroacetyl chloride.	by benzenesulphonyl chloride.
0.5	Trace	0.9	6.5	98.8
1.0	0.3	5.0	12.0	—
2.0	11.0	12.0	30.0	—
3.0	32.0	—	40.0	—
4.0	34.2	34.9	—	—
5.0	36.9	38.6	—	—
6.0	39.0	41.0	—	—

Now it is evident from the table that the rate of rearrangement of methylphenylketoxime by the different acid chlorides¹ is apparently dependent upon the strength of the acid from which a chloride has been derived, consequently more negative the acid residue coupled in methylphenylketoxime acyl ester greater the velocity of the change would be. The rearrangement of the same ketoxime, however, by

¹ *Loc. cit.*

acyl chloride from a weak acid such as acetic acid may be ascribed to the change of its acyl ester intermediately formed which must be brought about by the intervention of hydrochloric acid liberated in the reaction, since the acetyl ester does not apparently undergo rearrangement at all by heating itself at a high temperature, while it does readily as a matter of fact in the presence of hydrochloric acid. With regard to the question how hydrochloric acid may play a part in the rearrangement of the ketoxime acyl ester, we are further continuing an investigation, and expect to communicate the results in a short while.

2. The Rearrangement of Methylphenylketoxime Benzenesulphonyl Ester.

Methylphenylketoxime benzenesulphonyl ester, $(\text{CH}_3)(\text{C}_6\text{H}_5)\text{C:N}.\text{OSO}_2.\text{C}_6\text{H}_5$, was obtained by the action of benzenesulphonyl chloride upon the sodium salt of methylphenylketoxime prepared by the analogous method as suggested for that of diphenylketoxime.¹ It crystallizes in colourless needles and melts at 60–61°. Its analysis gave the following values for sulphur:

I	0.2039	gram.	substance	gave	0.1655	gram.	BaSO ₄ .
II	0.1850	"	"	"	0.1603	"	"
III	0.1748	"	"	"	0.1440	"	"
				Calculated for	Found.		
				$(\text{CH}_3)(\text{C}_6\text{H}_5)\text{C:N}.\text{OSO}_2.\text{C}_6\text{H}_5$.	I	II	III
Sulphur				11.60	11.10	11.90	11.32

The ester gradually changes to a thick oil owing to its molecular rearrangement, kept in a desiccator at ordinary temperature for 7–8 days in winter while for 1–2 days in summer. At the elevation of temperature to 81–82°, however, it undergoes rearrangement instantaneously with hissing noise changing at once into a brownish yellow viscid oil which is almost insoluble in ether and petroleum ether while readily in chloroform and acetone. The product of rearrangement or the oil was analysed, and we obtained the following values for sulphur:

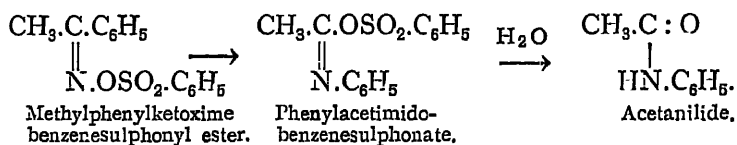
¹ These Memoirs, 1, 107 (1914), (p. 39).

I 0.2171 grm. substance gave 0.1752 grm. BaSO₄.
 II 0.1161 „ „ „ 0.0935 „ „

	Calculated for	Found.	
	CH ₃ C(OSO ₂ .C ₆ H ₅):N.C ₆ H ₅ .	I	II
Sulphur	11.60	11.06	11.07

The oil quickly decomposes by treating with water, depositing the characteristic scaly crystals of acetanilide (m. p. 112–113°), and does not give the original substance, methylphenylketoxime, and more by the action of alcoholic potash; hence it would be phenylacetimido-benzenesulphonate.

Now the change may, therefore, be represented as follows :



3. Synthesis of Phenylacetimido-benzenesulphonate.

It was synthesized from phenylacetimido-chloride¹ and silver benzenesulphonate². In this experiment the silver salt of benzenesulphonic acid dried at 150° was allowed to act upon phenylacetimido-chloride dissolved in acetone, producing a yellow solution. By driving out acetone by passing a current of dry air yellow oil was left as a residue, which was carefully washed with ether and then with petroleum ether. The oil so purified was analysed and gave following result :

0.3543 grm. substance gave 0.2607 grm. BaSO₄.

	Calculated for	Found.
	(CH ₃)(C ₆ H ₅)C(OSO ₂ .C ₆ H ₅):N.C ₆ H ₅ .	
Sulphur	11.60	10.10

The substance quickly decomposes by the action of water, producing acetanilide (m. p. 112–113°). It is identical in all respects with phenylacetimido-benzenesulphonate produced by rearrangement.

¹ Lieb. Ann., 184, 86 (1877).

² Ibid., 223, 244 (1884).

4. *The Action of the Ultraviolet Rays upon Methylphenylketoxime Benzenesulphonyl Ester.*

The ester was observed to change very likely to phenylacetimido-benzenesulphonate under rearrangement when exposed, in crystals or in the chloroform or alcoholic solution, to the action of the ultraviolet rays taking a mercury lamp as a source of light, while when a glass plate was interposed between the substance and the lamp no apparent change was observed to take place. In carrying out the experiment the crystals finely powdered were held in a thin layer between a pair of two quartz plates and then exposed to the ultraviolet rays. The following table shows the results of the experiment.

Time of exposure in minutes.	Change observed.
15	Somewhat yellowish.
30	Yellowish.
40	Yellow.
50	Brownish yellow.
65	Small oily drops visible.
100	Apparently oily form.
120	Brownish yellow oil.

5. *Conclusion.*

Interpreting from the results of the experiments thus stated, it may be concluded that all the facts so far observed with regard to the rearrangement of methylphenylketoxime are almost exactly concordant with the empirical rules found in connection with that of diphenylketoxime.

On the Beckmann Rearrangement. VII.

The Rearrangement of Ethyl-syn-benzhydroximic Acid by the Different Acid Chlorides, and of its Benzenesulphonyl Ester.

By

Mitsuru Kuhara and Fusao Ishikawa.

(Received April 20, 1916.)

One of us (M.K.) and Okada have brought forward from their works already performed as well as from those of other investigators an inference¹ that the presence of the acid residue linked to nitrogen is also one of the necessary conditions in the Beckmann rearrangement of the compounds of the hydroximic acid group, just as in the case of the ketoxime. Furthermore, the authors have examined the influence of the different acid chlorides upon the rate of rearrangement taking ethyl-syn-benzhydroximic acid as a representative, and all the phenomena exhibited in the changes of its benzenesulphonyl ester. The results of experiments show that the alkyl-syn-benzhydroximic acid and the ketoxime almost precisely follow the same rules for their rearrangement, consequently the facts which would support our view with regard to the Beckmann rearrangement of the oximido compounds have further been added.

1. The Rate of Rearrangement by the Different Acid Chlorides.

One gram of ethyl-syn-benzhydroximic acid, $C_6H_5.C(OC_2H_5):N.OH$, prepared according to the statement by Lossen² and an equivalent quantity of each of acetyl, monochloracetyl and benzenesulphenyl

¹ These Memoirs, 1, 1 (1914), (p. 19).

² Ber. D. Chem. Ges., 17, 1587 (1884); Lieb. Ann., 205, 235 (1880).

chlorides was dissolved in 15 cc. of chloroform and allowed to react to each other at 120–123° in a sealed tube for 3 hours. Removing the solvent by evaporation the residue was mixed with the 3% solution of sodium hydroxide and subjected to distillation. The aniline distilled over together with water by such a process was determined as its hydrochloride, as will be shown in the following table:

Acid chlorides used.	$C_6H_5.NH_2.HCl$ in gram.	$C_6H_5.NH_2$ in %.
Acetyl chloride	0.0710	4.7
Monochloroacetyl chloride	0.2422	31.0
Benzenesulphonyl chloride	0.4956	63.4

Now it is seen from the table that the rate of rearrangement of ethyl-syn-benzhydroxamic acid is likewise dependent upon the strength of the acid¹ from which a chloride has been derived. Such a relation, therefore, ought to be ascribed to the same cause as in the Beckmann rearrangement of the ketoxime.

2. *Ethyl-syn-benzhydroxamic Acid Benzenesulphonyl Ester and its Rearrangement.*

For preparing ethyl-syn-benzhydroxamic acid benzenesulphonyl ester, a certain quantity of ethyl-syn-benzhydroxamic acid² was dissolved in a solution of sodium hydroxide (2%) and an equivalent quantity of benzenesulphonyl chloride was added under vigorous shaking. The reaction then began with the evolution of heat, and after an hour with occasional shaking there separated out a white crystalline mass, which was crushed, then washed with water, dried and again washed with petroleum ether until no smell of benzenesulphonyl chloride was perceived. Now the whole mass was dissolved in a small quantity of ether and by adding petroleum ether to the solution ethyl-syn-benzhydroxamic acid benzenesulphonyl ester separated as a crystalline precipitate.

1 Zs. physik. Chem., 1, 73 (1887); J. prak. Chem., 28, 493 (1849).

2 *Loc. cit.*

The ester melts at 54–55°, and is soluble in chloroform, alcohol and benzene. By treating with alcoholic soda, it decomposes into its components, sodium benzenesulphonate separating out as crystals having pearly luster, while the sodium salt of hydroximic acid remains in the alcoholic mother liquor. The analysis of the ester gave the following values for sulphur :

I	0.2414	gram.	substance	gave	0.1615	gram.	BaSO ₄ .
II	0.3360	„	„	„	0.2570	„	„
	Calculated for				Found		
	$C_6H_5.C(OC_2H_5):N.OSO_2.C_6H_5$				I	II	
Sulphur	10.51				10.87	10.50	

Ethyl-syn-benzhydroximic acid benzenesulphonyl ester, when heated to 95°, was noticed to evolve some characteristic irritating smell of phenyl isocyanate with some change of colour, and on continuing heating up to about 150° the decomposition into phenyl isocyanate and benzenesulphonic acid ethyl ester took place instantaneously with violence. Subjecting the products of decomposition of the ester to the vacuum distillation a colourless liquid was isolated; the latter had the characteristic smell of phenyl isocyanate, and was found to boil at 166° (boiling point of phenyl isocyanate) at normal pressure. The liquid was also observed to change by heating with water into colourless crystals which melt at 234–235° after recrystallization from alcohol or ether. The formation of such a substance from phenyl isocyanate and water, and its melting point as well as its analysis show that it would be diphenylurea. Its analysis gave the following value for nitrogen :

0.1495 gram. substance gave 17.2 cc. N at 15° and 757 mm.

	Calculated for	Found
	$CO(C_6H_5.NH)_2$	
Nitrogen	13.21	13.51

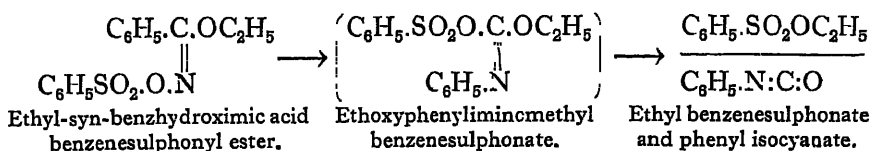
The residue left after the distillation of phenyl isocyanate was then boiled with water, by which process the decomposition of ethyl benzenesulphonate into its components took place. The aqueous part was neutralized with barium carbonate and the filtrate by evaporation deposited the crystals of barium benzenesulphonate which was confirmed by analysis :

I 0.1908 grm. substance gave 0.0919 grm. BaSO₄.

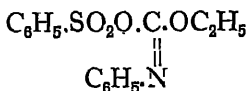
II 0.2567 „ „ „ 0.1275 „ „

Calculated for		Found	
(C ₆ H ₅ .SO ₂ O) ₂ Ba.H ₂ O		I	II
Barium	29.25	28.34	29.22

Interpreting from the results of experiments so far mentioned the nature of the change of ethyl-syn-benzhydroxamic acid benzenesulphonyl ester, it may be assumed that the ester would suffer the spontaneous Beckmann rearrangement simply at the elevation of temperature to 150°, but an intermediate product which ought to be ethoxyphenyliminomethyl benzenesulphonate, C₂H₅O.C(OSO₂.C₆H₅):N.C₆H₅, can not be isolated in the present case, as it may immediately decompose, possibly on account of its unstable nature in such a high temperature, into phenylisocyanate and ethyl benzenesulphonate¹ whose productions were confirmed by the formation of diphenylurea, benzenesulphonic acid and ethyl alcohol by the action of water upon the products of reaction. Thus the mechanism of decomposition may be represented in accordance with the following scheme :



By using pyridine, however, as a medium in the rearrangement of ethyl-syn-benzhydroxamic acid by the action of benzenesulphonyl-chloride, the authors have succeeded to isolate the intermediate product, ethoxyphenyliminomethyl benzenesulphonate,



In this experiment a certain quantity of ethyl-syn-benzhydroxamic acid was dissolved in anhydrous pyridine to which an equivalent quantity of benzenesulphonyl chloride was added, and the mixture heated at 65–70° for 5 hours over a water bath, the colour of the solution changing from yellow to reddish brown. The reaction product was then poured into dilute sulphuric acid, by which process the needle-shaped crystals and reddish yellow thick oil separated out.

¹ Refer the descriptions in "Beckmann's Rearrangement. III."—These Memoirs 1, 1 (1914), (p. 19).

The crystals and oil were severed by filtering through cotton wool, and the former purified by repeated recrystallization from alcohol was found to possess the melting point of 235° which corresponds to that of diphenylurea. The oil was treated with ether, and the ethereal solution, by evaporation, deposited the crystals of diphenylurea still mixed. Repeating the same process several times by dissolving the oil in ether and by evaporating the ethereal solution until no crystals appeared, almost pure oil was obtained. Its analysis gave the following values for sulphur :

I	0.2076 grm. substance gave 0.1461 grm. BaSO_4 .
II	0.1970 " " " 0.1551 " "
	Calculated for $\text{C}_6\text{H}_5\cdot\text{SO}_2\text{O}\cdot\text{C}(\text{:N}\cdot\text{C}_6\text{H}_5)\text{OC}_2\text{H}_5$
	Found
	I II
Sulphur	10.51 9.69 10.01

When the oil was heated to 150° , it suffered decomposition evolving the characteristic irritating vapour of phenyl isocyanate, while by treating with alkali and chloroform the disgusting smell of carbylamine. On allowing the oil to stand in contact with a dilute solution of alkali for a long while it partly changed into a solid mass from which diphenylurea was isolated.

By exposing ethyl-syn-benzhydroximic acid benzenesulphonyl ester to the ultraviolet rays, it seems to change first to ethoxyphenylimino-methyl benzenesulphonate which further decomposes into phenyl isocyanate and ethyl benzenesulphonate. Such an experiment was carried out in the same manner as in the case of ketoxime benzenesulphonyl esters, as mentioned in the previous articles,¹ and the results are as follows :

Time of exposure in minutes.	Changes observed.
10	Slightly coloured brownish yellow on surface.
20	Brownish yellow.
60	Somewhat oily form.
120	Oily state evolving the smell of phenyl isocyanate.

¹ These Memoirs, 1, 109 (1914), (p. 42).

3. Conclusion.

A conclusion is drawn from the results of experiments that the rearrangement of ethyl-syn-benzhydroximic acid by the different acid chlorides and of ethyl-syn-benzhydroximic acid benzenesulphonyl ester obeys the same rules as that of the ketoximes and of their benzenesulphonyl esters, excepting the decomposition of an intermediate product which progresses in somewhat different way on account of its unstability.

On the Beckmann Rearrangement. VIII.

By

Mitsuru Kuhara,

Naomichi Agatsuma and Kiukichi Araki.

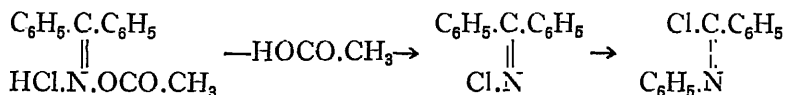
(Received Sept. 18, 1917).

I. *Function of Hydrochloric Acid in the Rearrangement of Acetyloximes.*

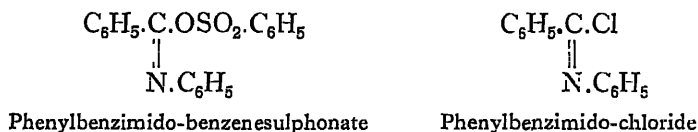
As a matter of fact it is true that the acyl ester of oxime which contains the acyloxyl radical derived from a strong acid such as benzenesulphonic acid spontaneously suffers the Beckmann rearrangement, while in the case of an ester containing the acyloxyl radical from a weak acid like acetic acid the rearrangement does not take place at all without the aid of hydrochloric acid.¹ Although in the latter case it has been noticed that hydrochloric acid actually takes part of rearrangement,² how it plays a rôle in reaction has not been fully explained as Stieglitz states³: "Beyond suggesting that the hydrochloric acid helps out the weak acetic acid residue in its tendency to exchange positions with the phenyl radical, Kuhara does not explain how the formation of the hydrochloride should facilitate the rearrangement." Recently the authors have, however, been led to declare that the rearrangement which acetyldiphenylketoxime undergoes under the influence of hydrochloric acid must be due practically to the migration of the chlorine radical derived from hydrochloric acid, but not of acetoxy, as it is highly probable that the chlorine in hydrochloric acid would replace acetoxy under the liberation of

- 1 Kuhara and Kainosho, Mem. Coll. Sci. Eng., Kyoto, 1, 254 (1903-1908) (p. 1); Kuhara and Todo, Ibid., 2, 337 (1909-1910) (p. 11); Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914) (p. 33); Kuhara and Watanabe, Ibid., 1, 349 (1916) (p. 47); Kuhara and Ishikawa, Ibid., 355 (1910) (p. 52).
- 2 Kuhara and Kainosho, Mem. Coll. Sci. Eng., Kyoto, 1, 254 (1903-1908) (p. 1); Henrich and Ruppenthal, Ber. D. Chem. Ges., 44, 1533 (1911).
- 3 Stieglitz and Stagner, J. Amer. chem. Soc., 38, 2056 (1916).

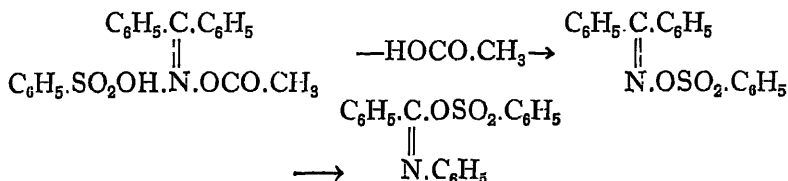
acetic acid. The scheme of rearrangement may, therefore, be shown as follows :



In such a course of reaction it is altogether impossible according to the previous works by one of us and his collaborators as already mentioned,¹ to isolate a chlorine compound in the form of chlorimido-benzophenone or phenylbenzimido-chloride, as the reaction progresses to the extreme thus far as to the formation of the final product, i.e., benzanilide, while by treating acetyldiphenylketoxime with benzenesulphonic acid which is nearly as strong as hydrochloric acid, the authors have succeeded to isolate phenylbenzimido-benzenesulphonate which corresponds to phenylbenzimido-chloride in constitution and other respects :



In the experiment equivalent quantities of acetyldiphenylketoxime and dehydrated benzenesulphonic acid were heated together to fusion, in which process an explosive violent reaction took place at 95-97° under the evolution of acetic acid, and the whole mass changed to a brownish yellow viscid liquid which was found to change instantly to benzanilide by the addition of water and to possess all other properties of phenylbenzimido-benzenesulphonate² obtained by the rearrangement of benzenesulphonyldiphenylketoxime as well as by synthesis. Thus, the reaction may be interpreted as follows :



Now it is no doubt that in such a reaction the benzenesulphoxyl group would take possession of the place of the acetoxyl radical, and

1 Loc. cit.

2 Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914) (p. 38).

then itself plays a part of rearrangement by its migration on account of its strong negativity; hence the action of hydrochloric acid upon acetylketoime for effecting its rearrangement may be assumed to be analogous to that of benzenesulphonic acid.

Further, the assumption that the movement of chlorine derived from hydrochloric acid would be a cause of rearrangement may also be supported by the rearrangement of the hydrochloride of oxime through dehydration. Kötze and Wunsdorf¹ mention that the hydrochlorides of acetoxime and acetophenoxime suffer the Beckmann rearrangement under the influence of heat, but no details are given in their article. Thus, the authors have conducted an analogous experiment by using the hydrochloride of diphenylketoxime² and have noticed that it changes instantly to benzanilide by heating at 128°, and also by passing dry hydrochloric acid gas through the fused diphenylketoxime at 125°. So, the formation of benzanilide in such experiments may be ascribed to the rearrangement of the chlorine compound formed by the dehydration of the hydrochloride of oxime, the reaction being highly probable to be analogous to that which would occur between acetyloxime and hydrochloric acid or benzenesulphonic acid, as will be seen in the following scheme:



In order to inquire after such a point of view, the action of dehydrating agents have been tried upon the hydrochloride of diphenylketoxime. For this purpose zinc chloride and chloral were taken; by using the former substance a greater part of the hydrochloride of diphenylketoxime changed into benzanilide at the temperature of 90°, while with the aid of the latter almost complete rearrangement took place in 10 minutes at 90°, but in 2 days at 25°.

Furthermore, the hydrochloride of diphenylketoxime methyl ether, $(\text{C}_6\text{H}_5)_2\text{C:N.OCH}_3.\text{HCl}$,³ has been observed by the authors to decompose into diphenylketoxime and methyl chloride by heating above its melting point 45°, without undergoing even a trace of rearrangement. Since in this case the methoxy group can not split up as alcohol by

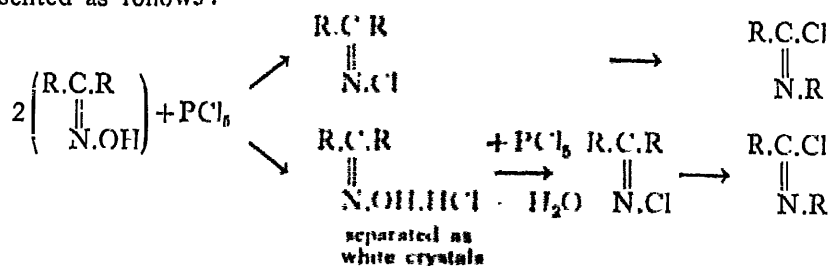
1 Kötze and Wunsdorf, J. prac. Chem., 88, 519 (1913).

2 Spiegler, Ber. D. Chem. Ges., 17, 812 (1884).

3 Ibid.

the action of hydrochloric acid but as methyl chloride, as is generally known, the formation of the chlorimido group >NCl which is assumed as a necessary factor of rearrangement would be impossible. Such a fact may, therefore, give a support indirectly in the favour of the view that the hydrochloride of diphenylketoxime would form chlorimido-diphenylketone as an intermediate product by dehydration.

According to Henrich and Ruppenthal¹ it is almost clear that hydrochloric acid actually enters into reaction in the Beckmann rearrangement of oxime by phosphorus pentachloride, its hydrochloride being formed as an intermediate product. Thus, gradually adding phosphorus pentachloride, as they state, to a solution of diphenylketoxime in absolute ether, the former at first disappears and then the hydrochloride of oxime separates out as white crystals. After the whole of a definite quantity (equivalent) of phosphorus pentachloride has been added there deposits a yellow chlorine compound which yields benzanilide by the action of water. The authors now interpret such a process of rearrangement as originating partly from the movement of the chlorine radical derived from phosphorus pentachloride by the substitution of the hydroxyl group in oxime and partly from that of the chlorine derived from the hydrochloride through dehydration by phosphorus pentachloride, that is, the rearrangement as being due to that of the chlorine compound containing the chlorimido group >NCl after all, thus the scheme of interpretation being represented as follows:



2. Rearrangement of Chlorimidodiphenylketone containing so called Hypochlorous Chlorine.

Peterson has obtained chlorimidodiphenylketone (chlorimidobenzophenone), $(\text{C}_6\text{H}_5)_2\text{C:N.Cl}$, by the action of hypochlorous acid upon imidodiphenylketone hydrochloride, $(\text{C}_6\text{H}_5)_2\text{C:NH.HCl}$, and also the

¹ Henrich and Ruppenthal: *Ber. D. Chem. Ges.*, **44**, 1533 (1911).

stereoisomeric chlorimides.¹ Stieglitz mentions² that "Kuhara's view that the weak negative character of the acetic acid residue is responsible for the rearrangement of acetylbenzophenonoxime without the aid of hydrochloric acid seems to be contradicted by the peculiar fact that all attempts to rearrange chlorimidobenzophenone, $(C_6H_5)_2C:NCl$, have failed to indicate the least trace of rearrangement," and also repeated in the following words³: "Chlorimidobenzophenone, $(C_6H_5)_2C:N.Cl$ has resisted every effort to effect its rearrangement and the same is true of the stereoisomeric chlorimides, $(C_6H_5)(XC_6H_4)C:N.Cl$. If the theory of direct exchange were correct, these substances, above all others, should show a spontaneous exchange of the aryl and halogen radicals. It is true, however, that it is still possible that the favorable medium has not yet been discovered for effecting the rearrangement of these compounds."

According to the authors' recent investigation, however, chlorimidobenzophenone prepared by the method suggested by Peterson⁴ seems in fact to suffer rearrangement through the action of alkali. Thus, by subjecting the mixture of chlorimidobenzophenone and caustic potash to fusion an explosive violent reaction took place, yielding a dark brown mass with the decomposition of a great part of the substance and at the same time evolving the dense fume of diphenylketone. The fused mass thus produced was then subjected to the steam distillation, and the distillate tested with a solution of bleaching powder which was observed to give distinctly the characteristic colour reaction of aniline although in a feeble state. Also the same product mixed with some alcohol and a few drops of chloroform was found to evolve the characteristic smell of isonitrile in a remarkable degree by heating.⁵ Trying the similar experiments, however, with diphenylketoxime and imidodiphenylketone (hydrochloride) which do not contain the chlorimido group, $:NCl$, there was no indication of their rearrangement at all, as even a trace of aniline has not been detected. Now it is in-

1 Peterson, *Amer. chem. J.*, **46**, 325 (1911).

2 Stieglitz and Stagner, *J. Amer. Chem. Soc.*, **38**, 2056 (1916). It is also stated by them that heat, bases, chlorine, phosphorus pentachloride have been tried (*ibid.*, foot note), and again by Vosburgh that five attempts were made to rearrange benzophenonechlorimide but all were unsuccessful (*ibid.*, 2094).

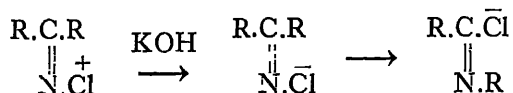
3 Stieglitz and Stagner, *J. Amer. Chem. Soc.*, **38**, 2059 (1916).

4 *Loc. cit.*

5 The authors have repeated Vosburgh's soda lime experiment (*loc. cit.*), but isonitrile has not been detected, while observed in the potash fusion.

conceivable that aniline could newly be built up from the products of decomposition, so it should be considered as being formed as the result of rearrangement; therefore, it may be concluded that chlorimidodiphenylketone would suffer rearrangement in which the presence of the chlorine linked to the nitrogen atom must be a necessary factor.

Such an unreadiness of the rearrangement of chlorimidodiphenylketone containing the hypochlorous chlorine may be explained by the assumption that its tendency to dissociate from the nitrogen atom would be too feeble, for its specific character is positive, while the chlorimidodiphenylketone supposed to contain the negative chlorine derived from phosphorus pentachloride or hydrochloric acid would suffer rearrangement with excessive readiness, so that it can not be isolated as an intermediate product.¹ The arrangement, therefore, which the chlorimidodiphenylketone containing the hypochlorous chlorine suffers by the alkali fusion must be ascribed to the change of the positive character of its chlorine to the negative under the influence of alkali. As soon as the chlorine radical gets the negative character, naturally its migration should instantly occur like the negative benzenesulphoxyl radical¹ with the simultaneous shifting of the phenyl group. So, it may be said that Kuhara's assumption respecting the movement of the negative radical would not be inconsistent with Stieglitz's electronic interpretation; now the authors have to represent the plan of rearrangement for the present as follows:



With regard to the rearrangement of the halogen imido esters (containing the hypochlorous chlorine) by alkali, one of us and Matsui³

1 Beckmann, Ber. D. Chem. Ges., 19, 988 (1886); 27, 300 (1894).

2 Stieglitz states in his electronic interpretation that the acyloxyl radicals in the oxime esters such as $(\text{C}_6\text{H}_5)_2\text{C}:\text{N}.\text{OCO}.\text{CH}_3$ and $(\text{C}_6\text{H}_5)_2\text{C}:\text{N}.\text{OSO}_2.\text{C}_6\text{H}_5$, take the positive charges like $\text{CH}_3.\text{CO}-\text{O}^+$ and $\text{C}_6\text{H}_5.\text{SO}_2-\text{O}^+$, and the rearrangements are assumed to "originate from the tendency of unstable positive atoms Cl^+ , $-\text{O}^+$, $=\text{N}^+$ to go over into their stable negative forms Cl^- , $-\text{O}^-$, N^- by capture of electron from other atoms in the same molecule a change which is effected in the rearrangement in question." Thus, if the change of the sign of the positive chlorine or acyloxyl radical were admitted to take place before or simultaneously with the exchange of radicals, the chlorine or acyloxyl radical which actually migrates should be considered to be practically negative as the authors assume.

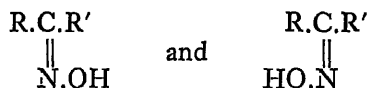
3 Kuhara and Matsui, Mem. Coll. Sci. Eng., Kyoto, 1, 187 (1902-1908).

have put forward an explanation based upon the assumption of Hoogewerff and van Dorp,¹ and Jones² has also explained the rearrangement of the halogen amides in the presence of alkali "in terms of copascular atomic hypothesis." But the authors' present case of the rearrangement of chlorimidobenzophenone by alkali does not stand in harmony with either of those explanations, so it seems to require an interpretation of some other type.

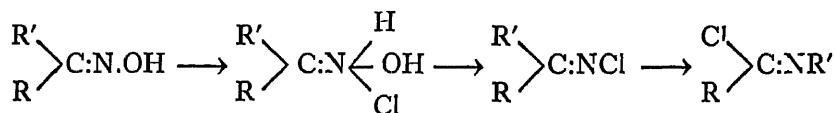
Furthermore, the authors have tried the alkali fusion of acetyldiphenylketoxime, but not a trace of aniline has been detected by the colour reaction; this shows that the acetoxyl radical being of the negative nature, may not change its sign by alkali, so the rearrangement would not take place on account of its weak negativity.

3. Relation of the Stereoisomerism of Oximes to their Products of Rearrangement.

It has been shown by Montagne³ and also by Jones⁴ that the theory of the monovalent nitrogen proposed by Stieglitz meets difficulties in explaining the differences observed in the migration of the hydrocarbon radicals, *R* and *R'*, of stereoisomeric oximes,



Thus, Stieglitz⁵ has recently brought forward a new interpretation for the rearrangement of oxime which is said by him to be the extension of the original theory, taking analogy with the rearrangement of triphenylmethylhydroxylamine by phosphorus pentachloride as will be seen in the following scheme:



But we may regard such an interpretation to be a modified form of the direct exchange theory, so both may be practically identical.

1 Hoogewerff and van Dorp, *Rec. trav. chim.*, **6**, 375 (1887); **8**, 173 (1889).

2 Jones, *Amer. chem. J.*, **48**, 25-26 (1912).

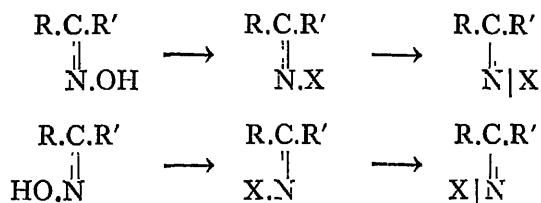
3 Montagne, *Ber. D. Chem. Ges.*, **43**, 2014 (1910).

4 Jones, *Amer. Chem. J.*, **48**, 23 (1912).

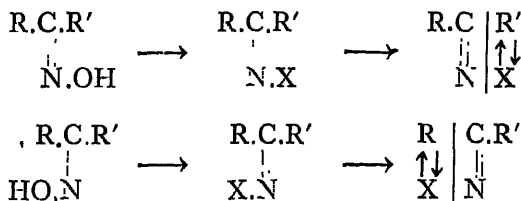
5 Stieglitz, *Ibid.*, **18**, 751 (1896).

6 Stieglitz and Leach, *J. Amer. Chem. Soc.*, **36**, 272 (1914).

Now if it is assumed in our direct exchange theory that the dissociation of acid residue in oxime ester which is regarded as a prime factor of rearrangement¹ as we assume, would occur before the migration of the hydrocarbon radical, R or R' , there should be no difference in the products of rearrangement as in the case of the monovalent nitrogen theory :



We have, however, a reason for believing that the exchange of the positions of the acid residue and hydrocarbon radical, R or R' , immediately opposite to the acid residue would take place *simultaneously*. Hence, if we admit such a view as correct the possibility of the different products of rearrangement could readily be explained :



Such a conception respecting the simultaneous occurrence of the mutual exchange of radicals originates, as will be seen, from the results of investigation on the rearrangement of the same acyl esters of the different ketoximes and of the different acyl esters of the same ketoxime :

1. It has been observed by one of us and his collaborators that the benzenesulphonyl esters of diphenyl², dibenzyl³ and dimethyl⁴ ketoximes suffer at once almost complete rearrangement at definite temperatures respectively, that is to say, conduct the exchange of radicals more or less readily according to the nature of the hydrocarbon radicals linked to the carbon atom of the diaryl or dialkyl methane

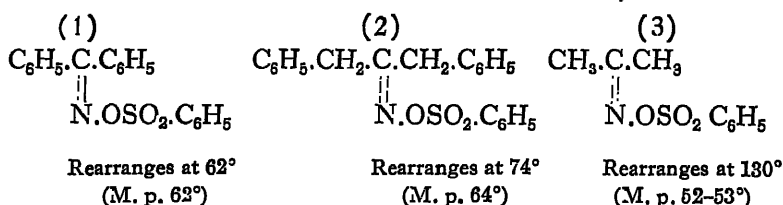
1 Loc. cit.

2 Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914) (p. 85).

3 See the experimental part.

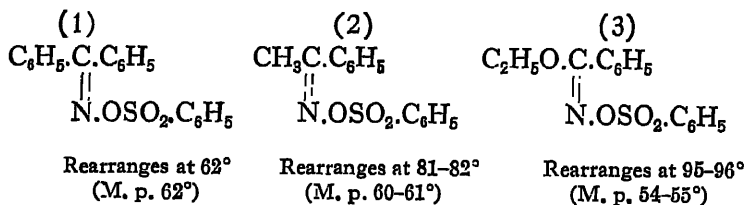
4 Ibid.

nucleus, judging from the structural point of view, namely in the order of phenyl, benzyl and methyl as will be seen :



Hence it is evident that the hydrocarbon radicals would exert some influence upon the migration of the benzenesulphoxyl group, since the latter moves more or less readily in the benzenesulphonyl esters of the different ketoximes, while the group, $>\text{C}\cdot\text{N}\cdot\text{OSO}_2\cdot\text{C}_6\text{H}_5$, is common to those oxime esters.

2. Comparing the rates of rearrangement of benzenesulphonyl esters of diphenylketoxime, phenylmethylketoxime and ethylsynbenzhydroximic acid in which the phenyl and benzenesulphoxyl groups equally occupy the positions directly opposite to each other :



it may be admitted as true that the rearrangement would occur more or less readily according to the nature of the hydrocarbon and alkoxyl radicals, that is, in the order of phenyl, methyl and ethoxyl linked to the same carbon atom with which the phenyl group directly opposite to the benzenesulphoxyl combines.

It may, therefore, be concluded that the phenyl, methyl and ethoxyl groups would exert an influence differently upon the movement of benzenesulphoxyl and phenyl immediately opposite to it, as the molecular structures of 3 esters are identical excepting 3 respective radicals, i.e., C_6H_5 , CH_3 and $\text{C}_2\text{H}_5\text{O}$.

3. Looking upon the rearrangement of several different acyl esters of diphenylketoxime whose acyloxyl groups have been derived from the acids of different strengths, such as *m*-nitrobenzenesulphonic, ben-

zenesulphonic, monochloroacetic and acetic acids,¹ it has also been noticed by one of us and his collaborators that they suffer rearrangement more or less readily according to the strength of the negative character of acyloxyl as will be shown in the following table:

<p>(1)</p> $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{C}_6\text{H}_5 \\ \\ \text{N} \cdot \text{OSO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2(m) \end{array}$ <p>Rearranges at 24° (M. p. 24°)</p>	<p>(2)</p> $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{C}_6\text{H}_5 \\ \\ \text{N} \cdot \text{OSO}_2 \cdot \text{C}_6\text{H}_5 \end{array}$ <p>Rearranges at 62° (M. p. 62°)</p>
<p>(3)</p> $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{C}_6\text{H}_5 \\ \\ \text{N} \cdot \text{OCO} \cdot \text{CH}_2\text{Cl} \end{array}$ <p>Rearranges above 195° (M. p. 140°)</p>	<p>(4)</p> $\begin{array}{c} \text{C}_6\text{H}_5 \cdot \text{C} \cdot \text{C}_6\text{H}_5 \\ \\ \text{N} \cdot \text{OCO} \cdot \text{CH}_3 \end{array}$ <p>Not rearranges (M. p. 71°)²</p>

So, the readiness and difficulty of exchange of radicals in the different acyl esters of diphenylketoxime are evidently dependent upon the strength of the negative character of the acyloxyl radical attached to the nitrogen atom, as the group $(\text{C}_6\text{H}_5)_2\text{C}:\text{N} \cdot$ is common to all of those acyl esrets.

Now a conclusion may be drawn as follows:

Since the acyloxyl and hydrocarbon radicals in the acyl esters of ketoximes are not independent from each other in partaking of rearrangement, but seem to exert mutually their influences for the exchange of their positions, the most conceivable assumption to be put forward is that *the exchange of radicals would be simultaneous*.

EXPERIMENTAL PART.

1. Action of Benzenesulphonic Acid upon Acetyldiphenylketoxime.

A mixture of equivalent quantities of acetyldiphenylketoxime and dehydrated benzenesulphonic acid was heated to fusion. Continuing

- 1 Kuhara and Todo, Mem. Coll. Sci. Eng., Kyoto, 2, 388 (1909-1910)(p. 11). *m*-Nitrobenzenesulphonic acid must be much stronger than benzenesulphonic acid, judging from its constitutional point of view.
- 2 Kuhara and Kainosho have found the melting point to be 71°, while Spiegler mentions as 55°. Mem. Coll. Sci. Eng., Kyoto, 1, 261 (1903-1908) (p. 1); Monatsh. Chem., 5, 205.

the heating the mixture suddenly changed into a dark yellow viscid mass at 95–97° with explosive violence under evolution of acetic acid. The product of reaction or viscid substance was treated with chloroform, by which process there was left some insoluble matter, giving a brownish yellow solution. The solution by evaporation gave a brownish yellow viscid liquid as a residue. The latter was observed to change at once into benzanilide by the action of water, and also showed the identity in other properties with phenylbenzimidobenzenesulphonate,¹ $C_6H_5.C(OSO_2.C_6H_5):N.C_6H_5$, obtained synthetically by the action of silver benzenesulphonate upon phenylbenzimidochloride as well as by the rearrangement of diphenylketoxime benzenesulphonyl ester. Further, it was noticed that diphenylketoxime itself suffers the similar change under the similar treatment with benzenesulphonic acid.

2. *Action of Heat and of Dehydrating Agents upon Diphenylketoxime Hydrochloride.*

Diphenylketoxime hydrochloride¹ was prepared by passing a slow current of hydrochloric acid gas through an ethereal solution of diphenylketoxime at 0°, separating out as white crystalline precipitate. The identification of the substance was made by its decomposition into components by the action of water, alkali or alkaline carbonate, and by its analysis.

0.289 grm. of the hydrochloride gave 0.172 grm. AgCl.

	Calc. as $(C_6H_5)_2C:N.OH.HCl$	Found
Chlorine	15.18	14.81

The hydrochloride fused at 128°, producing a colourless watery liquid, which on continuing the heating at the same temperature at first coloured slightly yellow evolving hydrochloric acid gas, and then changed at once into almost colourless crystalline mass under violent reaction. By repeating the recrystallization of the latter from aqueous alcohol we got the scaly crystals of pearly luster, which were confirmed to be benzanilide by its melting point and other properties. The same reaction was observed to take place at 125° by passing a current of hydrochloric acid into the heated oxime, producing 95% of the theoretical yield of benzanilide.

1 Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914) (p. 38).

2 Loc. cit.

With regard to the use of dehydrating agents the following experiments were carried out:

By heating a mixture of diphenylketoxime hydrochloride and finely powdered zinc chloride in a small flask immersed in a glycerine bath, it softened at about 60°. Now a part of contents of the flask was taken out and examined for benzanilide, but we could not recognize its production at all. Elevating the temperature, however, its production was observed with a gradual increase. Thus at 70° some was observed to have been produced, while at 90° almost whole of the hydrochloride to have suffered rearrangement.

By using chloral as a dehydrating agent, rearrangement was found to take place much more readily. In such a case diphenylketoxime hydrochloride was dissolved in a small quantity of chloral and the solution heated at 90° for 10 minutes, by which the colourless solution changed slightly yellow. Now after cooled, a solution of caustic soda was added in order to effect the decomposition of chloral. By warming the mixture chloroform produced was expelled, and the oxime escaped from reaction and sodium formate formed passed into solution, and benzanilide remained as precipitate which was separated by filtration, washed and recrystallized from aqueous alcohol. 0.378 grm. of the hydrochloride gave 0.287 grm. benzanilide, hence its yield was found to be 91% of the theoretical. It was also noticed that almost complete rearrangement took place when the mixture of the hydrochloride and chloral was kept at 25° in a thermostatt for two days and at a lower temperature for a week.

3. *Decomposition of the Hydrochloride of Diphenylketoxime Methyl Ether by Heat.*

Diphenylketoxime methyl ether, $(C_6H_5)_2C:N.OCH_3$, was prepared according to the method by Spiegler.¹ It was changed to its hydrochloride by passing a current of hydrochloric acid gas through its ethereal solution with a special precaution, as the hydrochloride is soluble in ether in presence of the excess of the acid.

By heating the hydrochloride above its melting point, it was noticed to decompose into diphenylketoxime and methyl chloride as is usually concerned of the compounds containing the mithoxyl group, and to show not a trace of the indication of rearrangement.

1 Loc. cit.

4. *Rearrangement of Chlorimidodiphenylketone.*

Chlorimidodiphenylketone (Chlorimidobenzophenone),¹ $(C_6H_5)_2C:NCl$, has been prepared according to Peterson's statement. By fusing an intimate mixture of chlorimidodiphenylketone and caustic potash each in finely powdered state, an explosive violent reaction took place yielding a dark brown mass under the decomposition of the greater part of the substance, and at the same time evolving a dense fume of benzophenone in a considerable quantity. A part of the reaction product was mixed with some alcohol and a few drops of chloroform, and then heating the mixture the characteristic smell of isonitrile was noticed in a remarkable degree. Now subjecting the same product to the steam distillation the aqueous distillate was observed to contain a small quantity of aniline, giving the characteristic violet colouration by the solution of bleaching powder although in a feeble state. The fume of benzophenone evolved in the reaction as above stated, when passed into water and tested with the bleaching powder solution, was also found to give the colour reaction of aniline.

Imidodiphenylketone hydrochloride, $(C_6H_5)_2C:NH.HCl$, diphenylketoxime, $(C_6H_5)_2C:NOH$ and acetyldiphenylketoxime, $(C_6H_5)_2C:N.OCO.CH_3$, however, under the similar treatment with caustic potash gave no reaction of aniline and isonitrile.

5. *Rearrangement of Dibenzylketoxime
Benzenesulphonyl Ester.*

Dibenzylketoxime, $(C_6H_5CH_2)_2C:N.OH$, prepared from dibenzylketone,² following the method of preparation of diphenylketoxime,³ was converted into its sodium salt by means of metallic sodium, and the salt thus obtained into benzenesulphonyl ester, $(C_6H_5CH_2)_2C:N.OSO_2.C_6H_5$ by the usual method as often described. The ester consists of colourless crystals and has been found to melt at 64° , being soluble in alcohol, benzene and chloroform. It was analysed and gave the following value for sulphur.

0.135 grm. substance gave 0.0864 grm. $BaSO_4$

Calc. for $(C_6H_5CH_2)_2C:N.OSO_2.C_6H_5$		Found
Sulphur	8.78	8.79

1 Loc. cit.

2 Apitzsch, Ber. D. Chem. Ges., 37, 1429 (1904).

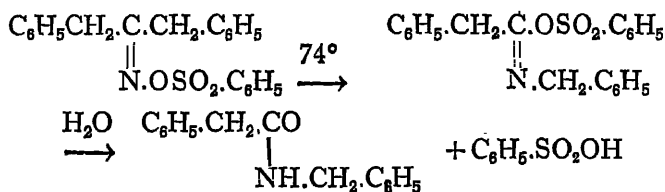
3 Loc. cit.

The ester changed into a yellow viscid liquid by gradual heating, while an explosive violent reaction spontaneously occurred at 74° under decomposition. The yellow viscid substance which consists mainly of the rearrangement product or benzylphenylacetimido-benzenesulphonate, $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{C}(\text{OSO}_2\cdot\text{C}_6\text{H}_5):\text{N}\cdot\text{CH}_2\text{C}_6\text{H}_5$, readily changed into benzylphenylacetamide, $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CONH}\cdot\text{CH}_2\text{C}_6\text{H}_5$, and benzenesulphonic acid by treating with water. Benzylphenylacetamide was confirmed by comparison with the melting point and other properties of the same substance especially prepared by the authors by synthesis, and benzenesulphonic acid by analysis of its barium salt.

0.268 grm. anhydrous barium salt gave 0.138 grm. BaSO_4 .

	Calc. for $(\text{C}_6\text{H}_5\cdot\text{SO}_2\text{O})_2\text{Ba}$	Found
Barium	30.42	30.30

Now the course of reaction would no doubt follow our rule as will be seen :



Benzylphenylacetamide has been synthetically prepared by the action of phenylacetyl chloride upon an ethereal solution of benzylamine. It crystallizes from alcohol in colourless scales and melts at $118\text{--}119^{\circ}$, and readily soluble in alcohol, slightly in ether and not in water. By heating with concentrated hydrochloric acid for a few hours in a sealed tube at $150\text{--}160^{\circ}$ it splits up into its components, i.e., phenylacetic acid and benzylamine. The substance gave the following value for nitrogen by analysis,

0.193 grm. substance gave 10.2 c.c. nitrogen at 15° and 765 mm.

	Calc. for $\text{C}_6\text{H}_5\text{CH}_2\cdot\text{CONH}\cdot\text{CH}_2\text{C}_6\text{H}_5$	Found
Nitrogen	6.22	6.27

The authors have also prepared acetyl and benzoyl esters of dibenzylketoxime, i.e., $(\text{C}_6\text{H}_5\cdot\text{CH}_2)_2\text{C}:\text{N}\cdot\text{OCO}\cdot\text{CH}_3$ and $(\text{C}_6\text{H}_5\text{CH}_2)_2\text{C}:\text{N}\cdot\text{OCO}\cdot\text{C}_6\text{H}_5$, by the similar method and studied their behaviours. Both are colourless crystalline substances, and soluble in alcohol, ether and chloroform. The acetyl ester melts at $33\text{--}34^{\circ}$ and the benzoyl at 60.5° . By heating they do not show an indication of rearrangement.

6. Rearrangement of Diphenylketoxime *m*-Nitrobenzenesulphonyl Ester.¹

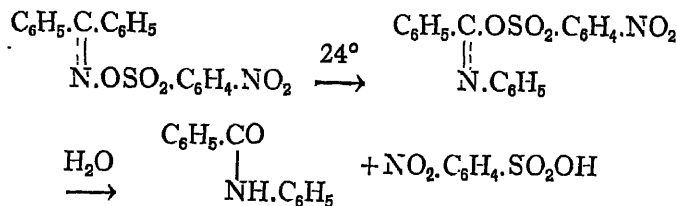
Diphenylketoxime *m*-nitrobenzenesulphonyl ester, $(C_6H_5)_2C:NOSO_2.C_6H_4.NO_2$, has been prepared from the sodium salt of diphenylketoxime by the action of *m*-nitrobenzenesulphonyl chloride² according to our method of preparation of the oxime esters.³ The substance crystallizes out when an ethereal solution of the reaction product has been evaporated by passing a current of dry air through it keeping the temperature below 24°. The substance was analysed and gave the following value for sulphur.

0.1354 grm. substance gave 0.0792 grm. BaSO ₄		
Calc. for $(C_6H_5)_2C:N.OSO_2.C_6H_4.NO_2$		
Sulphur	8.39	Found 8.03

The substance, melting at 24°, suffered the spontaneous rearrangement instantaneously with a hissing noise yielding a yellow viscid liquid like other oxime esters. The product of rearrangement or viscid substance, $C_6H_5.C(OSO_2.C_6H_4.NO_2):N.C_6H_5$, decomposed into benzanilide and *m*-nitrobenzenesulphonic acid quickly by treating with water, while slowly on allowing it to stand itself in open air. Of two products of decomposition, benzanilide has been identified by its properties, and *m*-nitrobenzenesulphonic acid⁴ by the analysis of its barium salt.

0.1844 grm. substance gave 0.077 grm. BaSO ₄ .		
Calc. for $(C_6H_4.NO_2.SO_2.O)_2Ba$		
Barium	24.54	Found 24.57

Thus, the course of rearrangement would be :



1 Unpublished work with Matsunami.

2 Limpricht, Lieb. Ann., 177, 65 (1875).

3 Loc. cit.

4 Limpricht, Lieb. Ann., 177, 60 (1872).

7. *Rearrangement of Dimethylketoxime Benzenesulphonyl Ester.*¹

Dimethylketoxime benzenesulphonyl ester, $(\text{CH}_3)_2\text{C}:\text{N}.\text{OSO}_2.\text{C}_6\text{H}_5$, has been prepared by Wege² by the action of benzenesulphonyl chloride upon dimethylketoxime in presence of aqueous alkali. The ester forms large colourless crystals and melts at 52–53°. By heating to 130° the reaction occurred with explosive violence under decomposition, and the product by treating with alkali liberated methylamine which was received in hydrochloric acid. The hydrochloride of methylamine was converted into platinum double salt, and analysed.

I.	0.092	gram.	double salt	gave	0.038	gram.	platinum.
II.	0.068	"	"	"	0.028	"	"
				Calc. for			Found
				$(\text{CH}_3.\text{NH}_2.\text{HCl})_2\text{PtCl}_4$	I	II	
Platinum				41.34	41.30	41.17	

Now it is evident that the ester has suffered rearrangement; but all the efforts to isolate methylacetamide which must be the product of rearrangement were unsuccessful.

8. *Rearrangement of Diphenylketoxime Chloracetyl Ester.*

Diphenylketoxime chloracetyl ester $(\text{CH}_3)_2\text{C}:\text{N}.\text{OCO}.\text{CH}_2\text{Cl}$, has been prepared by our method from the sodium salt of diphenylketoxime by the action of chloracetyl chloride. The ester forms colourless crystals and melts at 24°. It suffered rearrangement under decomposition by heating above 195°, and from the product of reaction benzanilide has been isolated.

1 Unpublished work with Yura.

2 Wege, Ber. D. Chem. Ges., 24, 3537 (1871).

On the Beckmann Rearrangement. IX.

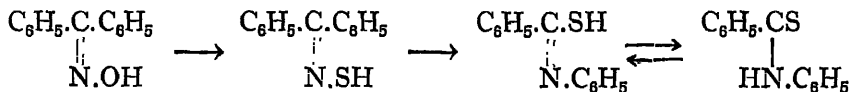
Actions of Phosphorus Pentasulphide upon Benzophenoxime.

By

Mitsuru Kuhara and Kôzô Kashima.

(Received June 27, 1919).

Dodge¹ states that he has obtained thiobenzanilide by the action of phosphorus pentasulphide upon the warm benzene solution of benzophenoxime, assuming that the reaction would be analogous to the Beckmann rearrangement. Also Ciusa² has conducted the similar experiment, expecting to prepare thiobenzophenoxime by the action of phosphorus pentasulphide upon the carbon bisulphide solution of benzophenoxime, but not succeeded to isolate the substance expected, while thiobenzanilide has been observed to be produced. He has, therefore, ascribed the reaction likewise to the Beckmann rearrangement of thiobenzophenoxime which is supposed to be formed in the intermediate stage of reaction, its primary cause being possibly due to the more acidic nature of sulphur than oxygen³; the scheme of reaction has been proposed as follows:



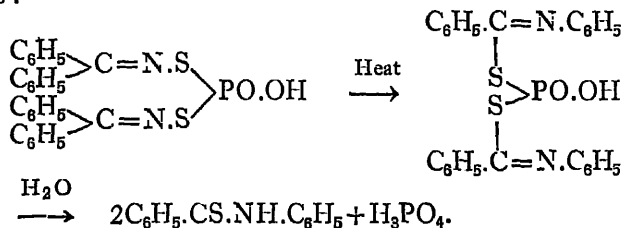
The authors have, however, noticed that the formation of thiobenzanilide from benzophenoxime by phosphorus pentasulphide may not be due to the direct rearrangement of thiobenzophenoxime, but seems to be dependent upon the rearrangement of phosphoryl ester of

1 Dodge, Lieb. Ann., 264, 184 (1891).

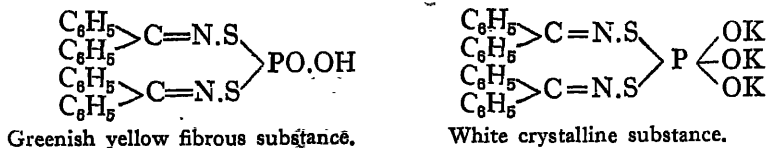
2 Ciusa, Chem. Centralbl., 1907, I, 23.

3 Sidgiwick, Org. Chem. of Nitrogen, (1910), p. 89.

thiobenzophenoxime which is possible to be formed as an intermediate product, just as one of us (M.K.) and his collaborators have ever noticed in the rearrangement of the acylesters of ketoximes, that is, standing in harmony with Kuhara's theory of migration of the negative acyloxyl radicals,¹ the scheme of rearrangement being represented as follows :

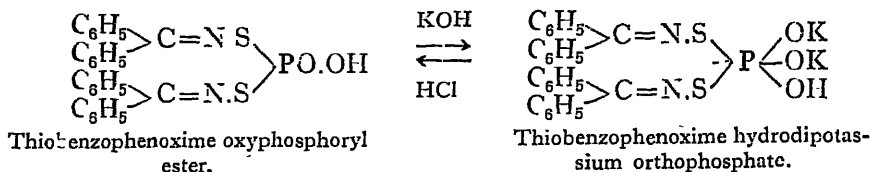


In the authors' experiment, benzophenoxime and phosphorus pentasulphide were allowed to act upon each other in proportion of 5 mols and 1 mol respectively with the addition of $1\frac{1}{2}$ mols phosphorus pentoxide, ether having been selected as solvent in order to keep the temperature of the mixture so low as to its boiling point (35°), while Dodge took benzene (boil. pt. 80°), and Ciusa carbon bisulphide (boil. pt. 46°). Driving off ether by passing the current of dry air through the ethereal solution, greenish yellow substance of fibrous structure was left as a residue, which by a slight elevation of temperature undergoes rearrangement with explosive violence. On account of such an explosive nature of the substance it was highly difficult to get in a perfectly pure state ; so the substance was treated with alcoholic potash, by which process a substance consisting of white crystalline powder was obtained and purified by the repeated recrystallization from ethyl acetate. This substance also undergoes rearrangement at 149° , but not so violently as the yellow substance. Consequently, the yellow and white substance seem to possess the following constitutions, inferred from the results of analysis and their properties :

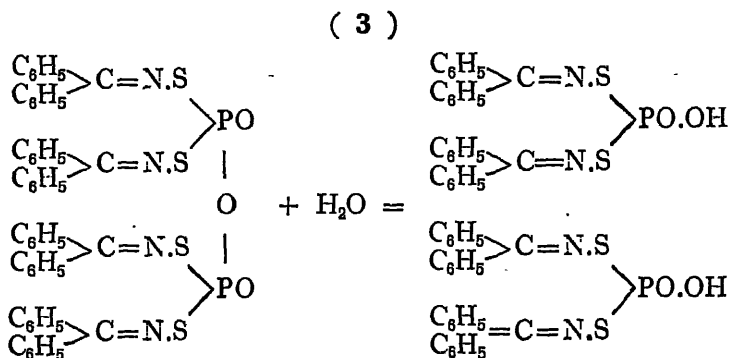
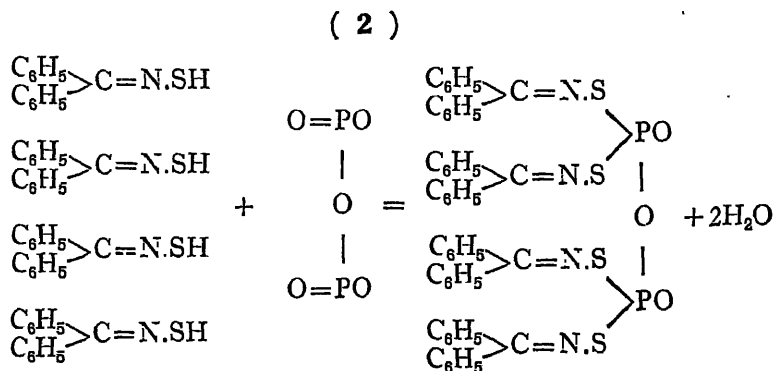
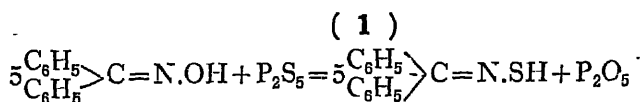


1 Kuhara and Kainosho, Mem. Coll. Sci. Eng., Kyoto, 1, 254 (1903-1908) (P. 1); Kuhara and Todo, Ibid., 2, 387 (1909-1910) (P. 11); Kuhara, Matsumiya and Matsunami, Mem. Coll. Sci., Kyoto, 1, 105 (1914) (P. 38); Kuhara and Watanabe, Ibid., 1, 349 (1916) (P. 47); Kuhara and Ishikawa, Ibid., 355 (1916) (P. 52); Kuhara, Agatsumo and Araki, Ibid., 3, 1 (1917) (P. 58).

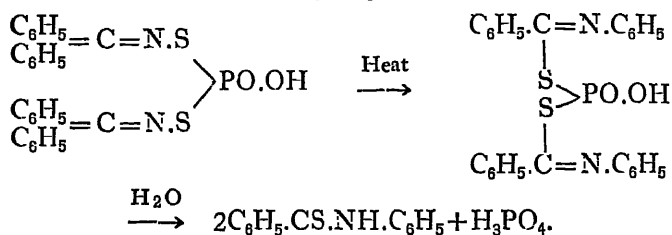
The white substance, on treating with hydrochloric acid, was found to retransform into the greenish substance; hence the two substances are mutually transformable, viz., one into the other by alkali and vice versa by acid:



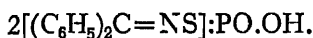
The authors have endeavoured to isolate thiobenzophenoxime, $(\text{C}_6\text{H}_5)_2\text{C}=\text{NSH}$, from those two substances by different possible ways, but not succeeded. Now they have to interpret the reactions regarding the formation of thiobenzanilide from benzophenoxime by the action of phosphorus pentasulphide as shown in the following scheme:



(4)



EXPERIMENTAL PART.

Thiobenzophenoxime Oxyphosphoryl Ester.

19 Grms. freshly prepared benzophenoxime dissolved in 600 c.c. of absolute ether was mixed with 4.4 grms. powdered phosphorus pentasulphide with the addition of 4.3 grms. phosphorus pentoxide, and the mixture was heated over a water bath with a reflux condenser for about six hours. Now the colourless ether was charged with greenish yellow colour; then the greater part of ether was removed by distillation, and its residual part driven off by passing a current of dry air through the solution, and finally sucked by pumping for removing the last trace of ether. By such a process of treatment there was left a greenish yellow substance of fibrous structure which is assumed to be thiobenzophenoxime oxyphosphoryl ester, and an intermediate product in the Beckmann rearrangement of the hypothetical thiobenzophenoxime. Its purification was exceedingly difficult on account of its excessive readiness of rearrangement.

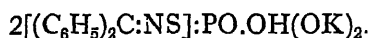
The determination of its molecular weight was, however, attempted with the crude substance by the cryoscopic method using benzene as solvent, expecting that its proximate value may be obtained so as to throw some light upon the nature of the substance:

	Grm. subst. taken	Lowering of the freez. point.		
I.	0.1151	0.085°		
II.	0.1846	0.132°		
Mol. weight calc. for		Observed values		
$2[(\text{C}_6\text{H}_5)_2\text{C}:\text{NS}]\text{PO.OH}$		I	II	Mean
488.5		395.9	408.5	402.4

The substance suffers rearrangement with an explosive violence

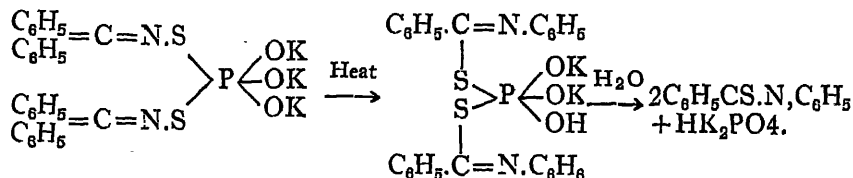
by mere heating to 70° , yielding a brownish yellow syrupy liquid with the evolution of a dense white fume. The syrup was dissolved in 10% aqueous solution of sodium hydroxide, and then by adding dilute hydrochloric acid the yellow precipitate produced. The latter was identified as thiobenzanilide by the melting point (98°) and other properties of the crystals deposited as thin plates from the alcoholic solution.

*Thiobenzophenoxime Hydrodipotassium
Orthophosphate.*



By treating thiobenzophenoxime oxyphosphoryl ester with alcoholic potash at ordinary temperature, it has changed to a white crystalline powder. As the latter is almost insoluble in common organic solvents, its purification was exceedingly difficult: so the authors took the simple method of washing the substance with several different solvents such as alcohol, ether, petroleum ether, benzene, etc., which may dissolve the admixed impurities. So roughly purified substance was found to dissolve particularly in ethyl acetate and to crystallize in white transparent needles. The substance is sparingly soluble in cold water and behaves like soap forming froth by shaking; this may indicate that the substance would be an alkaline salt of a complex organic acid or soap, standing in harmony with the constitution of the substance above shown.

It also undergoes rearrangement with violence by heating up to 149° , producing thiobenzanilide and phosphoric acid by treating the product with water; the scheme of reaction may be assumed to be:



The substance was analysed and the following results were obtained.

For the determination of carbon and hydrogen, the substance was ignited with lead chromate.

	Grm. subst. taken	Grm. CO ₂ found	Grm. H ₂ O found
I.	0.1363	0.2704	0.0343
II.	0.2019	0.3919	0.0588
III.	0.1548	0.3047	0.0497

For the determination of nitrogen, the substance was also ignited with lead chromate.

	Grm. subst. taken	C.c. Nitrogen found	Temp. and press. observed
IV.	0.1325	5.72	20° and 758.1 m.m.
V.	0.2442	10.50	20° and 757.8 m.m.
VI.	0.2742	12.10	19.5° and 754.3 m.m.

For the determination of sulphur the substance was oxidized with fuming nitric acid (sp. gr. 1.5) in a sealed tube, and sulphur estimated as BaSO₄ as usual.

	Grm. subst. taken	BaSO ₄ found
VII.	0.2000	0.1718
VIII.	0.4246	0.3807
IX.	0.5834	0.5210

For the determination of phosphorus, the substance was similarly treated as in the case of sulphur, and phosphorus estimated as magnesium pyrophosphate.

	Grm. subst. taken	Mg ₂ P ₂ O ₇ , found
X.	0.2525	0.0530
XI.	0.2135	0.0399

For the determination of potassium the substance was oxidized with fuming nitric acid in a sealed tube, and potassium estimated as its chloroplatinate.

	Grm. subst. taken	Grm. K ₂ PtCl ₆ , found
XII.	0.3887	0.2986
XIII.	0.4097	0.3454

The percentage composition of the substance is given in the following table.

Constitu- ents.	Calc. for $C_{24}H_{24}O_8$, $S_2N_2PK_2$	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	Mean
Carbon	53.58	54.11	52.94	53.69	—	—	—	—	—	—	—	—	—	—	53.58
Hydrogen	3.63	3.53	3.31	3.57	—	—	—	—	—	—	—	—	—	—	3.47
Nitrogen	4.81	—	—	—	4.98	4.95	5.00	—	—	—	—	—	—	—	4.98
Sulphur	11.01	—	—	—	—	—	—	11.82	12.28	12.24	—	—	—	—	12.17
Phosphorus	5.33	—	—	—	—	—	—	—	—	—	5.86	5.21	—	—	5.54
Potassium	13.42	—	—	—	—	—	—	—	—	—	—	—	12.33	13.26	12.79
Oxygen	8.24	—	—	—	—	—	—	—	—	—	—	—	—	—	7.47 (diff.)

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大正十五年八月二十五日印刷
大正十五年九月一日發行

京都帝國大學理學部生物化學研究室

編輯兼
發行者

小

松

茂

發行所 京都帝國大學理學部化學教室

神戸市江戸町一〇二

印刷者 田 中 守 一

神戸市江戸町一〇二

印刷所 田中印刷出版株式會社